Chapter 1

Concept Application Exercises

Exercise 1.1

Subjective Type

1. Mass of 1 atom of metal M $= \dfrac{54.94}{6.023 \times 10^{23}}$,

$$V = \frac{54.94}{6.023 \times 10^{23} \times 7.42} = 1.23 \times 10^{-23}\ \text{cm}^3$$

$$V = \frac{4}{3}\pi r^3 \Rightarrow 1.23 \times 10^{-23} = \frac{4}{3}\pi r^3$$

$\therefore r = 1.42 \times 10^{-8}$ cm

Objective Type

2. i. (2)

1. 1 mol S = 32 g,
2. $\dfrac{12 \times 3 \times 10^{23}}{6 \times 10^{23}} = 6$ g
3. 2 g atom of N = 28 g
4. 7.0 g Ag

ii. (2) mol of A $= \dfrac{50}{10} = 5$; mol of B $= \dfrac{50}{20} = 2.5$

A:B = 5:2.5 = 2:1,

Formula A_2B.

iii. 1. Weight of $H_2O = V \times d = 0.0018\ \text{mL} \times 1 = 0.0018$ g

$$n_{H_2O} = \frac{0.0018}{18} = 10^{-4}\ \text{mol} = 6.023 \times 10^{23} \times 10^{-4}$$

$$= 6.023 \times 10^{19}.$$

Fill in the Blanks Type

3. a. $\dfrac{18}{6.023 \times 10^{23}} = 3.0 \times 10^{-23}$

b. $n_{SO_2} = \dfrac{16}{64} = \dfrac{1}{4}$

Number of molecules $= \dfrac{1}{4} \times 6.023 \times 10^{23} = 1.5 \times 10^{23}$

c. $Na_2CO_3 = 2 \times 23 + 12 + 3 \times 16 = 106$ g

d. $n_{Ca(OH)_2} = \dfrac{196}{74} = 2.648 \approx 2.65$

$Eq_{Ca(OH)_2} = 2.65 \times 2 = 5.3$ (valency factor = 2)

e. $n_{H_3PO_4} = \dfrac{196}{98} = 2$, Eq $= 2 \times 3$ (tribasic acid) $= 6$

f. g atom or mol $= \dfrac{62}{31 \times 4} = 0.5$

g. g atom or mol $= \dfrac{24}{24} = 1$

Exercise 1.2

Subjective Type

1.

		Silica	H_2O	Impurities
% in original clay	$\Rightarrow$	a	12	$(88 - a)$
% after partial drying	$\Rightarrow$	50	7	43

On heating only water evaporates from clay, whereas silica and impurities are left as it is. Therefore, % ratio of silica and impurities remain unchanged, i.e.,

$$\frac{a}{50} = \frac{88 - a}{43}$$

$$a = 47.3\%$$

2.

$$Na_2CO_3 \xrightarrow{\Delta} \text{No change}$$

$$\underset{(2 \times 84\ g)}{2NaHCO_3} \longrightarrow Na_2CO_3 + \underbrace{CO_2\uparrow + H_2O\uparrow}_{\substack{(44\ g + 18 g) = 62\ g \\ \text{Weight loss}}}$$

Let x of Na_2CO_3 and $(2 - x)$ g of $NaHCO_3$ of

Weight lost on heating $NaHCO_3$ is due to CO_2 and H_2O

$\therefore 2 \times 84$ g $NaHCO_3 = 62$ g of weight lost

$$(2 - x)\ g\ NaHCO_3 = \frac{62(2 - x)}{2 \times 84} = 0.248$$

$\therefore x = 1.328$ g (weight of Na_2CO_3)

$$\%Na_2CO_3 = \frac{1.328 \times 100}{2} = 66.4\%$$

3. i. $d_{sol} = M\left(\dfrac{Mw_2}{1000} + \dfrac{1}{m}\right)$ (Mw_2 $NaNO_3 = 85\ \text{g mol}^{-1}$)

$$d = 1 \times \left(\frac{85}{1000} + \frac{1}{0.858}\right)$$

$$= 0.085 + 1.165 = 1.25\ \text{g mL}^{-1}$$

ii. $M(BaCl_2) = \dfrac{x \times 1000}{208 \times 250} = \dfrac{4x}{208}$ M of Ca^{2+} and

$\frac{2\times 4x}{208}$ M of $Cl^{\ominus}$

$$M(NaCl) = \frac{3.78\times 1000}{58.5\times 100} = 0.646\text{ M}$$

$$\frac{2\times 4x}{208} = 0.646,\ x = \frac{0.646\times 208}{8} = 16.8\text{ g}$$

4. i. $M = \frac{W_2\times 100}{Mw_2\times V_{sol}\text{ (in mL)}} = \frac{49\times 1000}{98\times 1000} = 0.5\text{ M}$

ii. $N = n\times M = 2\times 0.5 = 1.0$ m

iii. $m = \frac{W_2\times 1000}{Mw_2\times W_1}\ \begin{pmatrix} W_1 = V_{sol}\times d_{sol} - W_2 \\ = 1000\times 1.049 - 49 \\ = 1000\text{ g}\end{pmatrix}$

$$= \frac{49\times 1000}{98\times 1000} = 0.5\text{ m}$$

iv. $\chi_2 = \frac{W_2/Mw_2}{\frac{W_1}{Mw_1}+\frac{W_2}{Mw_2}} = \frac{49/98}{\frac{1000}{18}+\frac{49}{98}} = \frac{0.5}{55.5+0.5}$

$$= \frac{0.5}{56} = 0.009$$

5. NaCl does not react with HCl

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

mEq of Na_2CO_3 ≡ mEq of HCl

$$\equiv 50\times\frac{1}{10} = 5\text{ mEq per 25mL}$$

$$\equiv 50\text{ mEq per 250 mL}$$

Weight of $Na_2CO_3 = 50\times 10^{-3}\times\frac{106}{2} = 2.65$ g

% of $Na_2CO_3 = \frac{2.65}{4.0}\times 100 = 66.25\%$

6. i. Total mEq of acid = 500 × 2 + 100 × 2 × 2 (*n* factor)

= 1000 + 400 = 1400

Total mEq of monoacid alkali = 1000

Acid left after neutralisation with alkali

= 1400 – 1000 = 400 mEq

N of acid left $= \frac{400\text{ mEq}}{(500+100)\text{ mL}} = \frac{400}{600} = 0.66$ N

ii. mEq of acid ≡ mEq of Na_2CO_3

30 mL × 0.66N = 20 mL × N Na_2CO_3 ...(ii)

Strength of $Na_2CO_3{\cdot}x\,H_2O = 143\text{ g L}^{-1}$

$$M_{Na_2CO_3\cdot xH_2O} = \frac{\text{Strength}}{Mw} = \left(\frac{143}{106+18x}\right)$$

$$M_{Na_2CO_3\cdot xH_2O} = \left(\frac{2\times 143}{106+18x}\right)\ (n\text{ factor} = 2)$$

Substitution the value of N of $Na_2CO_3.\ x\ H_2O$ in Eq. (i), we get

$$30\times 0.66 = 20\times\left(\frac{2\times 143}{106+18x}\right)$$

Solve for x

$x = 10.16 \approx 10$

So water of crystallisation of $Na_2CO_3{\cdot}xH_2O = 10$

Formula: $Na_2CO_3{\cdot}10H_2O$

Objective Type

7. i. (1) $\frac{Mw\text{ of }X_4O_6}{\text{Atomic weight of 4X}} = \frac{\text{Weight of }X_4O_6}{\text{Weight of X}}$

$$\frac{4x+96}{4x} = \frac{10}{5.72}$$

$x = 32$

ii. (1) Use the formula

$$109 = \left(100+\frac{18x}{80}\right)\%$$

x = 40% free SO_3.

Mass of H_2SO_4 = 100 – 40 = 60 g

Moles of $SO_3 = \frac{40}{80} = 1/2\ (q)$

Moles of $H_2SO_4 = \frac{60}{98}\ (p)$

$$\left(\because\frac{p-q}{p+q}\right) \Rightarrow \frac{\frac{60}{98}-\frac{1}{2}}{\frac{60}{98}+\frac{1}{2}} \approx \frac{1}{9}$$

iii. (1) (*n* factor for $O_2 = 4$)

Volume strength of $H_2O_2 = \frac{24}{4} = 6$ L

6 'VS' of H_2O_2 = 1 N H_2O_2

6 'VS' of H_2O_2 × Vol of H_2O_2 = Vol of O_2

'VS' of H_2O_2 × 100 cm^3 = 3 dm^3

'VS' of H_2O_2 × 0.1 dm^3 = 3dm^3

'VS' of H_2O_2 = 30 dm^3 or L

6 'VS' of H_2O_2 = 1 N

30 'VS' of $H_2O_2 = \frac{1\times 30}{6} = 5$ N

$M = 5/2 = 2.5$

iv. (4) Moles of S $= \frac{4}{32} = \frac{1}{8} = 0.125$ mol

$S + O_2 \longrightarrow SO_2$

$SO_2 + Cl_2 \longrightarrow 2Cl^{\ominus} + SO_4^{2-}$

$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^{\ominus}$

Moles of S = Moles of SO_2 = Moles of SO_4^{2-} = Moles of $BaSO_4$ = 0.125 mol.

v. (4) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

Initial mol ratio of H_2/O_2 = 2:1

Mol ratio required in the reaction = 3/1.5

= 2:1

Since the mol ratio is same, so none is th limiting reagent.

vi. (1) $Hg^{2+} \equiv 4I^{\ominus} = HgI_4^{2-}$

$1 \text{ mol} \equiv 4 \text{ mol} \equiv 1 \text{ mol}$

$\frac{1}{4} \text{ mol} \equiv \frac{4}{4} \text{ mol} = \frac{1}{4} \text{ mol}$

$= 0.25 \text{ mol}$

8. i. (3), ii. (4), iii. (4), iv. (3), v. (1, 2), vi. (3), vii. (4), viii. (4), ix. (2), x. (1)

i. (3) Since the molarity of glucose has to be increased (from 0.01 M to 0.02 M), so this can be carried out either by evaporating the solution or by adding some more glucose.

So, the only possible answer is (3).

I. Evaporate 50 mL of solution

mmoles of glucose initially $= 0.01 \times 200 = 2$

Volume after evaporation $= 200 - 50$

$= 150 \text{ mL}$

$$M_{\text{glucose}} = \frac{\text{mmoles}}{V_{\text{mL}}} = \frac{2}{150} = 0.013 \text{ M}$$

II. mmoles of glucose added $= \frac{0.180}{180} \times 1000 = 1$

Total mmoles of glucose $= 2 + 1 = 3$

Volume $= 150$ mL (after evaporation of 50 mL solution)

$$M_{\text{glucose}} = \frac{3}{150} = 0.02 \text{ M}$$

III. Add 50 mL of water:

New volume of solution $= 200 + 50 = 250$ mL

$$M_{\text{glucose}} = \frac{2 \text{ mmol}}{250 \text{ mL}} = 0.008 \text{ M}$$

Hence answer is (c).

ii. (4) $63.546 = \frac{a \times 63 + (100 - a) \times 65}{100}$

$a = 72.7\,\% \approx 73\%$

iii. (4) $m = \frac{\chi_2 \times 1000}{(1 - \chi_2) \times Mw_1}$

$$3 = \frac{\chi_2 \times 1000}{(1 - \chi_2) \times 18}$$

Solve for $x_2 = 0.05$

iv. (3) $M_1V_1 = M_2V_2$

$0.2 \text{ M} \times 1 \text{ mL} = M_2 \times 1000 \text{ mL}$

$M_2 = 2 \times 10^{-4}$

$\therefore N = 2 \times 2 \times 10^{-4} = 4 \times 10^{-4}$

v. (1, 2) Temperature-dependent quantities are those which involve volume, since the volume of solution changes on temperature. So, M and N are temperature-dependent.

vi. (3) $M_1V_1 = M_2V_2 \left(M = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2} \right)$

$$V_1 \times \frac{90 \times 10 \times 1.8}{98} = 0.2 \times 1 \text{ L}$$

$V_1 = 0.012 \text{ L} = 12 \text{ mL}$

vii. (4) Loss in weight is due to nH_2O.

$\therefore (142 + 18n)$ g of $Na_2SO_4 \cdot nH_2O = 18n$ g of loss in weight of H_2O

$$100 \text{ g of } Na_2SO_4 \cdot nH_2O = \frac{18n \times 100}{142 + 18n}$$

$$\therefore \frac{18n \times 100}{142 + 18n} = 55.9$$

Solve for $n \Rightarrow n = 9.99 \approx 10$

viii. (4) 0.02 mol HCl $= 0.02$ of $H^{\oplus} + 0.2$ mol of $Cl^{\ominus}$

0.01 mol $BaCl_2 = 0.1$ mol of $Ba^{2+} + 0.1 \times 2$ mol of $Cl^{\ominus}$

Total $Cl^{\ominus} = 0.4$ mol.

Total volume $= 500 \text{ mL} = \frac{1}{2}$ L

$$\therefore [Cl^{\ominus}] = \frac{0.4}{1/2} = 0.8 \text{ M}$$

ix. (2) $d_{\text{sol}} = M\left(\frac{Mw_2}{1000} + \frac{1}{m}\right)$

$$1.0585 = 1 \text{ M}\left(\frac{58.5}{1000} + \frac{1}{m}\right)$$

Solve for m

$m = 1.0$

Note: *When $d_{sol} \approx 1$, $M = m$. Do not solve such questions. Give direct answer.*

x. (1) $V_1 + V_2 = 2 \text{ L}$ ...(i)

$N_1V_1 + N_2V_2 = N_3V_3$

$0.5 \times V_1 + 0.1 \times V_2 = 0.2 \times 2$

$0.5V_1 + 0.1V_2 = 0.4$ ...(ii)

Solve Eqs. (i) and (ii)

$V_1 = 0.5 \text{ L}, V_2 = 1.5 \text{ L}$

9. i. (2), ii. (2), iii. (2), iv. (4)

i. (2) Mw of $NaH_2PO_4 = 120$ g (it is dibasic) (valency factor = 2)

Eq of NaOH = Eq of NaH_2PO_4

$(n = 1)$ $(n = 2)$

$$1\, M \times 1 \times V_L = \frac{12}{120} \times 2.$$

$V_L = 0.26 \text{ L} = 200 \text{ mL}$

ii. (2) $SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

$$\left.\begin{array}{r} 1 \text{ mol } H_2SO_4 \equiv 2NaOH \\ 2 \text{ mol } HCl \equiv 2NaOH \end{array}\right] = 4 \text{ mol NaOH}$$

$$\left.\begin{array}{r} 1 \text{ mol } H_2SO_4 \equiv 1 \text{ mol } Ba(OH)_2 \\ 2 \text{ mol } HCl \equiv 1 \text{ mol } Ba(OH)_2 \end{array}\right] \Rightarrow 2 \text{ mol } Ba(OH)_2$$

iii. (2) mEq of $H_2SO_4 = 100 \times 0.2 \times 2 = 40$

mEq NaOH $= 100 \times 0.2 \times 1 = 20$

mEq of H_2SO_4 left $= 40 - 20 = 20$

Total volume $= 100 + 100 = 200$ mL

$$N \text{ solution} = \frac{20 \text{ mEq}}{200 \text{ mL}} = 0.1 \text{ N}$$

iv. **(4)** Total mEq of HCl = 100 × 0.1 = 10

Total mEq of NaOH = 30 × 0.2 = 6

mEq of HCl left = 10 – 6 = 4

mEq of HCl = mEq of KOH

$4 = 0.25 \times V; \quad V \Rightarrow 16$ mL

Fill in the Blanks Type

10. a. 84, 32 **b.** 100% **c.** 44.8 mL **d.** 2.16 g

a. Ew of $NaHCO_3 = \frac{84}{1}$ (valency factor = 2)

Ew of $SO_2 = \frac{64}{2} = 32$ (valency factor = 2)

b. $2Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$

2 mol 1 mol

The percent yield of CO_2 is 100% whether $Ca(HCO_3)_2$ is 100% pure or 50% pure.

c. $K_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2KCl$

1 mol 1 mol

$$M_{K_2SO_4} = \frac{5 \times 1000}{174 \times 250} = \frac{20}{174}$$

$M \times V_L\,(K_2SO_4)$ = moles of $BaSO_4$

$$\frac{20}{174} \times V_L = \frac{1.2}{233}$$

$V_L = 0.0448$ L = 44.8 mL

d. $Ag_2CO_3 \longrightarrow 2Ag + CO_2\uparrow + O_2\uparrow$

(Mw = 276 g) (2 × 108 g)

The residue is due to Ag.

276 g of Ag_2CO_3 = 2 × 108 g Ag

$$2.76 \text{ g of } Ag_2CO_3 = \frac{2 \times 108 \times 2.76}{276} = 2.16 \text{ g}$$

11. a. $$m = \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

$$1.05 = \frac{W_2 \times 1000}{95 \times 750} \qquad \therefore W_2 = 74.8 \text{ g}$$

b. [Mw $(C_{12}H_{22}O_{11})$ = 342 g]

$$\% \text{ of sugar} = \frac{W_2}{W_1 + W_2} \times 100 = \left(\frac{1000}{1000 + 2000}\right) \times 100$$

$$= 1000/3$$

$$\% \text{ of } H_2O = \left(\frac{W_1}{W_1 + W_2}\right) \times 100 = \left(\frac{2000}{3000}\right) \times 100$$

$$= 200/3$$

$$\chi_1\,(H_2O) = \frac{2000/18}{\frac{2000}{18} + \frac{1000}{342}} = \frac{111.11}{111.11 + 2.92}$$

$$= \frac{111.11}{114.03} = 0.97$$

χ_2 (sugar) = 1 – 0.97 = 0.03

12. a. Eq of NH_3 =

$$\frac{\text{Volume of a gas at STP}}{\text{Volume of 1 equivalent of gas}} = \frac{2.24}{22.4} = 0.1 \text{ equivalent}$$

mEq of $NH_3 = 0.1 \times 10^3 = 100$

mEq of $H_2SO_4 = 100 \times N$

mEq of $H_2SO_4 \equiv$ mEq of NH_3

$100 \times N \equiv 100$

$N_{H_2SO_4} = 1$

$$M_{H_2SO_4} = \frac{1}{2} = 0.5 \text{ M}$$

b. mEq of $MCO_3 \equiv$ mEq of H_2SO_4

$$\left[\frac{0.84}{Ew\,(M) + Ew\,(CO_3^{\ 2-})}\right] \times 10^3 = 40 \times \frac{1}{2}$$

$$\left(\frac{0.84}{E + \frac{60}{2}}\right) \times 10^3 = 20$$

$$\left(\frac{0.84}{E + 30}\right) = \frac{20}{1000}$$

$E = 12$

Ew of metal carbonate = 12 + 30 = 42

c. Mw of $(COOH)_2 \cdot nH_2O = 90 + 18n$

$$\left[\begin{matrix}\text{Eq of } (COOH)_2 \cdot nH_2O \\ \text{in 250 mL solution}\end{matrix}\right] = \left(\frac{1.575}{90 + 18n}\right) \times 2$$

(n factor = 2) ...(i)

mEq of acid = mEq of NaOH

$$16.68 \text{ mL} \times N = 25 \times \frac{1}{15}$$

N(acid) = 0.099 ≈ 0.1 Eq L^{-1}

$$= \frac{0.1 \times 250}{1000} \qquad \text{...(ii)}$$

$$= \frac{0.1}{4} \text{ Eq per 250 mL}$$

Equating Eqs. (i) and (ii), we get

$$\left(\frac{2 \times 1.575}{90 + 18n}\right) = \frac{0.1}{4}$$

Solve for n, $n = 2$

Formula: $(COOH)_2 \cdot 2H_2O$

d. mEq H_3PO_4 = mEq of NaOH

25 mL × N = 40 mL × 0.1 N

N of $H_3PO_4 = 0.16$

$$N = \frac{W_2 \times 1000}{Ew_2 \times \text{vol}_{\text{sol}}} \quad (Mw\ H_3PO_4 = 98,\ Ew = \frac{98}{3}$$

(n factor = 3)

$$0.16 = \frac{W_2 \times 1000}{98/3 \times 250}, \quad \text{Wt } H_3PO_4 \text{ mL}^{-1} = 1.32 \text{ g mL}^{-1}$$

$$d_{H_3PO_4} = \frac{W_2}{\text{vol}} = \frac{1.32}{1 \text{ mL}} = 1.32 \text{ g mL}^{-1}$$

e. Mw of $Ca(OH)_2 = 74$ g

$$Ew \text{ of } Ca(OH)_2 = \frac{74}{2} = 37\text{g}$$

$$N_{Ca(OH)_2} = \frac{\% \text{ by weight} \times 10 \times d}{Ew_2}$$

$$= \frac{1.48 \times 10 \times 1.025}{37} = 0.41$$

mEq of $Ca(OH)_2 \equiv$ mEq of HCl

$25 \text{ mL} \times 0.41 \text{ N} \equiv 0.1 \times V_{HCl}$

$V_{HCl} = 102.5$ mL

Exercises

Single Correct Answer Type

1. (2) Mw_2 of $CaCO_3 = 40 + 12 + 48 = 100$

$$\text{Moles of } CaCO_3 \text{ in 10 g} = \frac{10}{100}$$
$$= 0.1 \text{ mol} = 0.1 \text{ g atom}$$

2. (2) $p_{O_2} = P_{Total} \times \chi_{O_2}$ (mole fraction of O_2)

$$\chi_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{N_2} + n_{CO_2}}$$

$$\chi_{O_2} = \frac{0.76 \times 10^{20}}{(0.76 + 0.50 + 6.08) \times 10^{20}} = \frac{0.76}{7.34}$$

$$p_{O_2} = P_{Total} \times \chi_{O_2} = 734 \times \frac{0.76}{7.34}$$
$$= 76.0 \text{ mm of Hg.}$$

3. (3) $M_1V_1 + M_2V_2 = M_3V_3$

$(V_3 = V_1 + V_2)$

$1.5 \times 480 + 1.2 \times 520 = M_3 \times 1000$

$M_3 = 1.344$ M

4. (2) $$\frac{Ew \text{ of acid}}{Ew \text{ of salt of Mg}} = \frac{\text{Weight of acid}}{\text{Weight of salt}}$$

$Mg + 2HCl$ (monobasic acid) $\rightarrow MgCl_2 + H_2$

Let Ew of acid = Ew of H + Ew of acid radical

$\therefore$ Ew of salt of Mg = Ew of Mg + Ew of acid radical

$$\therefore \frac{Ew \text{ of acid}}{Ew \text{ of Mg salt}} = \frac{\text{Weight of acid}}{\text{Weight of Mg salt}}$$

$$\Rightarrow \frac{Ew \text{ of H} + Ew \text{ of acid radical } (E)}{Ew \text{ of Mg} + Ew \text{ of acid radical } (E)} = \frac{1.0}{1.301}$$

$$\Rightarrow \frac{1 + E}{12 + E} = \frac{1.0}{1.301}$$

$\therefore E = 35.54$

$\therefore$ Ew of acid = Ew of H + Ew of acid radical

$= 1 + 35.54 = 36.54$

5. (1) 1 mol of O_2 = 4 eq. of O

22400 mL of O_2 = 4 eq. of O

$$46.6 \text{ mL of } O_2 = \frac{4}{22400} \times 46.6$$
$$= 0.00832 \text{ eq.}$$

Equivalent of metal = Equivalent of O

$$\frac{\text{Weight}}{Ew} = 0.00832$$

$$\frac{0.1}{E} = 0.00832$$

$$\therefore E = \frac{0.1}{0.00832} = 12.0$$

6. (2) Mw of metal chloride $(MCl_x) = M + x \times 35.5$

$= 2 \times VD = 2 \times 39.5$

$= 79.0$

$Mw = Ew \times x$

Valency of metal $= x$

Atomic weight of element = $Ew \times x$

$MCl_x = 3.82 \times x + x \times 35.5 = 79$

$$x = \frac{79}{3.82 + 35.5} \approx 2$$

Atomic weight = $Ew \times x = 3.82 \times 2 = 7.64$

7. (1) Let the formula of oxide = $M_2O_x = 44$

$2 \times M + x \times 16 = 44$

$2(E \times x) + x \times 16 = 44$

$2(14 \times x) + 16x = 44$

$\therefore x = 1$

Atomic weight $= 14 \times 1 = 14$

8. (1) Moles $\propto$ Pressure

i. $$\frac{2}{Mw_A} \propto 1 \text{ atm}$$

Pressure of B = 1.5 – 1 = 0.5 atm

ii. $$\frac{3}{Mw_B} \propto 0.5 \text{ atm}$$

$$\frac{3}{Mw_B} \times \frac{Mw_A}{2} = \frac{0.5}{1}$$

$$\frac{Mw_A}{Mw_B} = 0.5 \times \frac{2}{3} = \frac{1}{3}$$

$\therefore Mw_A : Mw_B = 1:3$

9. (2) $$\text{Moles of Fe} = \frac{0.0056}{56} = 10^{-4} \text{ mol}$$

1 mol of alum = 2 mol of Fe

2 mol of Fe = 1 mol of alum

$$10^{-4} \text{ mol of Fe} = \frac{1}{2} \times 10^{-4} \text{ mol}$$
$$= 0.5 \times 10^{-4} \text{ mol}$$

10. (1) i. $X + 2Y \longrightarrow XY_2$

0.1 mol of XY_2 = 10 g

1 mol of XY_2 = 100 g

ii. $3X + 2Y \longrightarrow X_3Y_2$

0.05 mol of $X_3Y_2 = 9$g

$$1 \text{ mol of } X_3Y_2 = \frac{9}{0.05} = 180 \text{ g}$$

$$\left.\begin{array}{l} \therefore X + 2Y = 100 \\ 3X + 2Y = 180 \end{array}\right] \begin{array}{l} MwXY_2 = 100 \\ MwX_2Y_3 = 180 \end{array}$$

Solve for X and Y

$X = 40$ g

$Y = 30$ g

11. (1)

$$\text{Moles of AlCl}_3 \text{ produced} = \frac{6.67}{133.5} = 0.05 \text{ mol}$$

$$\text{Excess of Al} = \frac{0.54}{27} = 0.02 \text{ mole}$$

g atom or moles of Al taken = 0.05 + 0.02 = 0.07

g atom or moles of Cl_2 taken = 3 × 0.05 = 0.15

12. (1) Total HCl ⇒ 25 × 1 = 25 mEq

Excess HCl ⇒ 5 × 1 = 5 mEq

HCl used ⇒ 25 − 5 = 20 mEq

∴ mEq of HCl = mEq of carbonate

$$\frac{20}{1000} \text{ Eq} = \frac{\text{Weight}}{Ew} \text{ of carbonate} = \frac{1}{Ew}$$

$$\therefore Ew = \frac{1000}{20} = 50$$

13. (4) $N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$

$(V_4 = V_1 + V_2 + V_3 + V_4)$ or

V_4 = Final volume = 1 L ≡ 1000 mL

$$5 \times N + 20 \times \frac{N}{2} + 30 \times \frac{N}{3} = N_4 \times 1000$$

$$\therefore N_4 = \frac{N}{40}$$

14. (1) Since two H-atoms are replaced

$$\therefore Ew = \frac{Mw}{n} = \frac{98}{2} = 49$$

15. (3) Moles or molecules of $O_2{:}N_2 = \frac{1}{32} : \frac{4}{28}$

$$= \frac{1}{32} : \frac{1}{7} = \frac{7}{32} : 1 = 7{:}32$$

16. (1) $3\,BaCl_2 + 2Na_3PO_4 \longrightarrow 6NaCl + Ba_3(PO_4)_2$

[3 mol   2 mol   6 mol   1 mol]

Given ⇒ 0.5 mol of $BaCl_2$ and 0.2 mol of Na_3PO_4

To find the limiting reagent:

2 mol of Na_3PO_4 ⇒ 3 mol of $BaCl_2$

0.2 mol of Na_3PO_4 ⇒ 0.3 mol of $BaCl_2$

∴ Na_3PO_4 is the limiting reagent

∴ 2 mol of Na_3PO_4 ⇒ 1 mol of $Ba_3\,(PO_4)_2$

0.2 mol of Na_3PO_4 ⇒ 0.1 mol of $Ba_3(PO_4)_2$

17. (1) 3 mmol   1 mmol   3 mmol   2 mmol

$$3Pb(NO_3)_2 + Cr_2(SO_4)_3 \rightarrow 3PbSO_4 \downarrow + 2Cr(NO_3)_3$$

50 × 0.1   50 × 0.05

= 5 mmol   = 2.5 mmol

First find the limiting reagent.

3 mmol of $Pb(NO_3)_2$ ⇒ 1 mmol of $Cr_2(SO_4)_3$

$$5 \text{ mmol of } Pb(NO_3)_2 \Rightarrow \frac{1}{3} \times 5$$

$$\Rightarrow \frac{5}{3} = 1.66 \text{ mmol}$$

So $Pb(NO_3)_2$ is the limiting reagent.

i. 3 mmol of $Pb(NO_3)_2$ ⇒ 3 mmol of $PbSO_4$

5 mmol of $Pb(NO_3)_2$ ⇒ 5 mmol

$$\Rightarrow \frac{5}{1000} \text{ mol} \Rightarrow 0.005 \text{ mol}$$

ii. Species left in the solution are $Cr_2(SO_4)_3$ and $Cr(NO_3)_3$.

To calculate the concentration of $Cr_2(SO_4)_3$:

Initial mmol = 2.5

Reacted mmol = 1.65

Left mmoles = 2.5 − 1.66 = 0.84 mmol

Total Volume = 50 + 50 = 100 mL

$$\text{Concentration} = \frac{0.84}{100} = 0.0084 \text{ M}$$

iii. To calculate the concentration of $Cr(NO_3)_3$:

3 mmol of $Pb(NO_3)_2$ ⇒ 2 mmol of $Cr(NO_3)_3$

$$5 \text{ mmol of } Pb(NO_3)_2 \Rightarrow \frac{2}{3} \times 5$$

$$\Rightarrow \frac{10}{3} = 3.33 \text{ mmol}$$

$$\text{Concentration} = \frac{3.33}{100} = 0.033 \text{ M}$$

18. (1, 2) Acceptable value = 52.57 °C

Maximum uncertainty = 52.5 °C

19. (1) Ew of metal chloride = Ew of M + Ew of Cl

= 12 + 35.5 = 47.5

47.5 g of metal chloride ⇒ Weight of metal ⇒ 12 g

$$0.475 \text{ g of metal chloride} \Rightarrow \frac{12 \times 0.475}{47.5}$$

⇒ 0.12 g

20. (1) 22400 mL = 1 mol of CO_2 = 2 Eq of CO_2

11200 mL = 1/2 mol of CO_2 = 1 Eq of CO_2

= 1 Eq of CO_3^{2-}

Weight of metallic carbonate that would produce 1 g equivalent or 22 g or 11.2 L of CO_2 at STP would be its Ew.

$$Ew \text{ of metallic carbonate} = \frac{4.2 \times 11200}{1120} = 42 \text{ g}$$

Ew of metal = Ew of MCO_3 − Ew of CO_3^{2-}

$= 42 - 30 = 12$

$$\left[Ew \text{ of } CO_3^{2-} = \frac{60}{2} = 30\right]$$

Alternatively:

$22400 \text{ mL} = 1 \text{ mol of } CO_2 = 2 \text{ Eq } CO_3^{2-}$

$11200 \text{ mL} \Rightarrow 1 \text{ Eq of } CO_3^{2-}$

$$\therefore 1120 \text{ mL} \Rightarrow \frac{1}{11200} \times 1120 = 0.1 \text{ Eq of } CO_3^{2-}$$

$\text{Eq of } MCO_3 = \text{Eq of } CO_3^{2-}$

$$\frac{\text{Weight}}{Ew} = \frac{\text{Weight}}{Ew} = 0.1 \text{ Eq}$$

$$\therefore 0.1 = \frac{4.2}{Ew \text{ of } MCO_3}$$

$\therefore \text{Eq of } MCO_3 = 42$

$\therefore Ew \text{ of M} = Ew \text{ of } MCO_3 - Ew \text{ of } CO_3^{2-}$

$= 42 - 30 = 12$

21. (1) $1 \text{ mol of } H_2 = 22400 \text{ mL} = 2 \text{ Eq of } H_2$

$1 \text{ Eq of } H_2 = 11200 \text{ mL}$

$$\text{Eq of } H_2 = \frac{560}{11200} = \frac{1}{20} \text{ Eq}$$

[Let the weight of A be x g; weight of B $= 0.5 - x$]

Eq of A + Eq of B = Eq of H_2

$$\frac{x}{12} + \frac{0.5 - x}{9} = \frac{1}{20}$$

$\therefore \quad x = 0.2$

$$\% \text{ of A} = \frac{0.2 \times 100}{0.5} = 40\%$$

% of B = 60%

22. (2) Specific heat × Atomic weight = 6.4

(Dulong and Petit law)

$$\text{Atomic weight} = \frac{6.4}{\text{specific heat}} = \frac{6.4}{0.25}$$

Atomic weight $= Ew \times$ valency $= 25.6$

$$\text{Valency} = \frac{\text{Atomic weight}}{Ew} = \frac{25.6}{12} = 2$$

(Valency is always a whole number)

23. (3) $\begin{bmatrix} \text{Rutile} = TiO_2 \\ \text{Cassiterite} = SnO_2 \end{bmatrix}$ Both are isomorphous

Mw of $TiO_2 = x + 32$

$(x + 32)$ g of $TiO_2 \Rightarrow 32$ g of oxygen

$$100 \text{ g of } TiO_2 \Rightarrow \frac{32}{(32 + x)} \times 100$$

$$\therefore \frac{32 \times 100}{(32 + x)} = 39.95$$

$\therefore x = 48.10$

24. (2) Weight of salt = 13.4 g

Weight of $H_2O = 6.3$ g

Weight of anhydrous salt = 13.4 – 6.3 = 7.1 g

$$\text{Moles of anhydrous salt} = \frac{7.1}{842} = 0.05$$

$$\text{Moles of } H_2O = \frac{6.3}{18} = 0.35 \text{ mol}$$

0.05 mol of anhydrous salt ⇒ 0.35 mol of H_2O

$$1 \text{ mole of anhydrous salt} \Rightarrow \frac{0.35}{0.05} = 7 \text{ mol}$$

25. (2) Since no water added, so volume of solution cannot exceed 2 L. So, less concentrated solution should be taken in its total volume.

Only the small portion of more concentrated solution is to be mixed, so that the total concentrated is less than (0.3 M HCl).

Let x L of 0.3 M solution is mixed.

Total volume $= (x + 1)$ L

$M_1V_1 + M_2V_2 = M_3V_3 \qquad [V_3 = (1 + x) \text{ L}$

$0.3 \times x \text{ L} + 0.15 \times 1 \text{ L} = M_3 (1 + x) \text{ L}$

Final molarity = 0.2 M

$0.3x + 0.15 = 0.2(1 + x)$

$x = 0.5$ L

Maximum volume = 1 + 0.5 = 1.5 L

26. (1) 4 g of NaOH = 4/40 = 0.1 mole = 100 mmol ≡ 100 mEq

HCl = 500 × 1 = 500 mEq

$$N \text{ of } H_2SO_4 = \frac{W_2 \times 1000}{Ew_2 \times V_{\text{sol}} \text{ (in mL)}}$$

or

$$= \frac{\% \text{ by weight} \times 10 \times d}{Ew_2}$$

$$= \frac{49 \times 10 \times 1.1}{49} = 11 \text{ N}$$

mEq of H_2SO_4 = 11N × 10.00 mL = 110 mEq

Total acid = 110 + 500 = 610 mEq

NaOH = 100 mEq

Acid left = 610 – 100 = 510 mEq

Total volume = 1000 mL

$$\text{Normality of solution} = \frac{\text{mEq}}{\text{mL}} = \frac{510}{1000} = 0.51 \text{ N}$$

27. (1) $$\frac{\text{Molecular weight of } X_4O_6}{\text{Atomic weight of 4 X}} = \frac{\text{Weight of } X_4O_6}{\text{Weight of X}}$$

$$\frac{4x + 96}{4x} = \frac{10}{5.72}$$

$x = 32$

28. (4) Weight of Cl reacted = 12.7 – 5.6 – 7.1 g

7.1 g Cl ≡ 5.6 g of metal

35.5 g Cl = 28 g of metal

29. (3) Use formula

$$d = M\left(\frac{Mw_2}{1000} + \frac{1}{m}\right) \Rightarrow 1.8 = 18\left(\frac{98}{1000} + \frac{1}{m}\right)$$

Solve for m:

$\therefore m = 500$

30. (2) Temporary hardness is due to $HCO_3^{\ominus}$ of Ca^{2+} and Mg^{2+}

$$Ca(HCO_3)_2 + \underset{56\text{ g}}{CaO} \longrightarrow \underset{(2 \times 100)\text{ g}}{2\,CaCO_3} + H_2O$$

0.56 g CaO $\equiv 2$ g $CaCO_3$ in 10 L H_2O

$= 2$ g $CaCO_3$ in 10^4 mL H_2O

$= 200$ g $CaCO_3$ in 10^6 mL H_2O

31. (3) $3Mg(OH)_2 + 2H_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 3H_2O$

$$\frac{3 \times 58.3}{2 \times 98} = \frac{100}{W}, \quad \therefore W = 112\text{ g}$$

32. (2) X: 50% Y: 50%

X : Y = 5 : 2.5 = 2 : 1, hence X_2Y.

33. (1) Total weight of alcohol and water

$= 10 \times 0.7893 + 20 \times 0.9971$

$$\text{Volume of mixture} = \frac{10 \times 0.7893 + 20 \times 0.9971}{0.9571}$$

$= 29.08$ mL

Change in volume $= (20 + 10) - 29.08$

$= 0.92$ mL

$$\%\text{ change in volume} = \frac{0.92 \times 100}{30} = 3.06\%$$

$\approx 3.1\%$

34. (2) $$\text{Molality} = \frac{1000 \times \text{Weight of solute}}{Mw \times \text{Weight of solvent}}$$

$$9 = \frac{1000 \times W}{98 \times 910}$$

$W = 802.6\text{ g L}^{-1}$

$= 80.26$ g per 100 mL

35. (2) Use formula

$$d = M\left(\frac{Mw_2}{1000} + \frac{1}{m}\right) \Rightarrow 1.0585 = 1\left(\frac{58.5}{1000} + \frac{1}{m}\right)$$

Solve for m :

$\therefore m = 1$

36. (2) Na_2SO_4 does not react.

N (NaOH) $= 0.1 = 4\text{ g L}^{-1}$

$= 0.4$ g per 100 mL

37. (3) 4 g sulphur is in 100 g compound, hence 32 g sulphur is in $= \left(\frac{100}{4} \times 32\right) = 800\text{g}$ compound

38. (3) Mol. ratio O_2:N_2

$$\frac{1}{32} : \frac{4}{28}$$

$$\text{Molecules } \frac{N_A}{32} : \frac{4N_A}{28} \Rightarrow 7 : 32$$

39. (2) $$\frac{0.116\text{ g of A}}{116\text{ g }(Mw\text{ A})} = \frac{0.074\text{ of }Ca(OH)_2}{W\,[Ca(OH)_2]}$$

$W = 74\text{ g} \equiv 1\text{ mol } Ca(OH)_2 \equiv 2\text{ mol } (\overset{\ominus}{O}H) \equiv 2\text{ mol } (H^{\oplus})$

40. (3) Na_2SO_3:$H_2O \equiv 50{:}50$ (Mw of $Na_2SO_3 = 126$)

$$\text{Mole: } \frac{50}{126} : \frac{50}{18}$$

Ratio: 1:7

41. (1) Na_2CO_3 is not affected by heating.

$$2NaHCO_3 \longrightarrow \underset{\text{Residue}}{Na_2CO_3} + H_2O + CO_2$$

42. (3) $$\chi_2 = \frac{n_2}{n_1 + n_2} = 0.25 \text{ (ethanol) (solute) } (Mw_2 = 46\text{ g})$$

$$\chi_1 = \frac{n_1}{n_1 + n_2} = 0.75 \text{ (water) (solvent) } (Mw_1 = 18\text{ g})$$

$$\frac{\chi_1}{\chi_2} = \frac{n_1}{n_2} = \frac{3}{1} \Rightarrow \frac{W_1 \times Mw_2}{Mw_1 \times W_2} = \frac{3}{1}$$

$$\frac{W_1 \times 46}{18 \times W_2} = 3$$

$$\frac{W_1}{W_2} = 1.17$$

$$\therefore \frac{W_2}{W_1 + W_2} = 0.46$$

43. (1) $N_2 \equiv 2NH_3 \equiv 3H_2 \equiv 6H$

$$Ew \text{ of } N_2 = \frac{x_2}{6} = y_2$$

$$Ew \text{ of } NH_3 = \frac{2x_1}{6} = y_1$$

$$\therefore y_1 - y_2 = \left(\frac{2x_1}{6} - \frac{x_2}{6}\right) = \left(\frac{2x_1 - x_2}{6}\right)$$

44. (4) $\because 9.108 \times 10^{-31}$ kg of electrons contain

$$= \frac{1}{6.023 \times 10^{23}}\text{ mol}$$

$\therefore$ 1 kg of electron will contain

$$= \frac{1}{6.023 \times 10^{23} \times 9.108 \times 10^{-31}}$$

$$= \frac{1}{6.023 \times 9.108} \times 10^8\text{ mol}$$

45. (1) Weight of 6.023×10^{23} (Avogadro's number) = Mw of $CuSO_4{\cdot}5H_2O = 249$ g

$= 1$ mol of $CuSO_4{\cdot}5H_2O$

Weight of 1×10^{22} molecules of $CuSO_4{\cdot}5H_2O$

$$= \frac{249 \times 1 \times 10^{22}}{6.023 \times 10^{23}} = 4.14\text{ g}$$

46. (4) Balance the equation:

$$2CrO_5 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2O + \frac{7}{2}O_2$$

$$2 \text{ mol } CrO_5 \Rightarrow \frac{7}{2} \text{ mol of } O_2$$

$$1 \text{ mol } CrO_5 \Rightarrow \frac{7}{4} \text{ mol of } O_2$$

47. (3) Balance the equation:

$$\underset{1 \text{ mmol}}{BrO_3^{\ominus}} + \underset{5 \text{ mmol}}{5Br^{\ominus}} \longrightarrow \underset{1 \text{ mmol}}{3Br_2} + 3H_2O$$

Given: $50 \times 0.1 = 5$ mmol $30 \times 0.5 = 15$ mmol

$Br^{\ominus}$ is the limiting reagent.

5 mmol of $Br^{\ominus}$ gives $\Rightarrow$ 3 mmol of Br_2

$$15 \text{ mmol of } Br^{\ominus} \text{ gives} \Rightarrow \frac{3 \times 15}{5} = 9 \text{ mmol}$$

$$= 9 \times 10^{-3} \text{ mol}$$

48. (2) i. Moles of NaOH = 1.0 M × 1.5 L = 1.5 mol

Moles of H_2SO_4 = 1.0 M × 1L = 1.0 mol

$$\underset{2 \text{ mol}}{2NaOH} + \underset{1\text{mol}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$$

Moles of H_2SO_4 reacted with NaOH

$$= \frac{1}{2} \text{ mol of } H_2SO_4$$

$$= \frac{1}{2} \times 1.5 = 0.75 \text{ mol } H_2SO_4$$

$$\% \text{ purity of } H_2SO_4 = \frac{0.75 \text{ mol} \times 100}{1.0 \text{ mol}} = 75\%$$

ii. For slope: $\frac{x}{a} + \frac{y}{b} = 1$

$$\text{Slope}\left(\frac{y}{x}\right) = \frac{-b}{a} = -\frac{1.5}{1.5} = -1$$

49. (2) Let the volume of solution = 1 L

Weight of solution = 1 × $d = d$ g

Number of moles of solute (n_2) in 1 L solution = M

$$\therefore \frac{W_2}{Mw_2} = M$$

W_2 (weight of solute) = $M \times Mw_2$

W_1 (weight of solvent) = Weight of solution – Weight of solute

$$= (d - M \times Mw_2)$$

Number of moles of solvent (n_1)

$$= \frac{W_1}{Mw_1} = \left(\frac{d - M \times Mw_2}{Mw_1}\right)$$

$$\therefore \chi_2 = \frac{n_2}{n_1 + n_2} = \frac{M}{\left(\frac{d - M \times Mw_2}{Mw_1}\right) + M}$$

$$= \frac{M \times Mw_1}{M(Mw_1 - Mw_2) + d}$$

50. (3) 1 mol $H_2SO_4 \equiv 2$ mol $H_3O^{\oplus} \equiv 1$ mol SO_4^{2-}

$$\left(\frac{100}{1000} \times 0.1 = 0.01\right) \equiv 2 \times 0.01 + 0.01 = 0.03 \text{ mol}$$

$$\text{Total number of g ions} = 0.03 \times 6.02 \times 10^{23}$$

$$= 0.18069 \times 10^{23}$$

51. (2) $2N_2 + 3O_2 \longrightarrow 2N_2O_3$, (% yield = 80%)

$$\text{Initial mol of } N_2 = \frac{7.0}{28} = 0.25 \text{ mol}$$

$$\text{Moles of } N_2 \text{ converted} = 0.25 \times \frac{80}{100} = 0.2$$

2 mol N_2 = 3 mol O_2

0.2 mol N_2 = 0.3 mol O_2 (1 mol O_2 = 2 oxygen atom)

= 2 × 0.3 mol O atom

= $2 \times 0.3 \times 6.02 \times 10^{23} = 3.6 \times 10^{23}$

52. (4)

$$M = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2} = \frac{36.5 \times 10 \times 1.2}{36.5} = 12 \text{ M}$$

$$m = \frac{36.5 \times 1000}{36.5 \times (100 - 36.5)} = \frac{1000}{63.5} = 15.7\,m$$

53. (4)

$$\underset{\substack{10 \times 1 \\ = 10 \text{ mmol}}}{BaCl_2} + \underset{\substack{5 \times 0.5 \\ = 2.5 \text{ mmol}}}{K_2SO_4} \longrightarrow BaSO_4\downarrow + 2KCl$$

Here, K_2SO_4 is the limiting reagent

1 mmol $K_2SO_4 \equiv 1$ mmol $BaSO_4$

2.5 mmol $K_2SO_4 \equiv 2.5$ mmol $BaSO_4$

$$\equiv \frac{2.5}{1000} = 0.0025 \text{ mol } BaSO_4$$

54. (1) $\chi_B = 0.2$; $\chi_A = 0.1$

$$m = \frac{\chi_B \times 1000}{\chi_A \times Mw_A} = \frac{0.2 \times 1000}{0.8 \times 18} = 13.88$$

55. (3)

$$\underset{(\text{excess})}{3NaOH} + \underset{\substack{100 \text{ mL} \\ 1 \text{ mmol}}}{FeCl_3} \longrightarrow \underset{\equiv 1 \text{ mmol}}{Fe(OH)_3} + 3NaCl$$

$FeCl_3 \equiv Fe(OH)_3$

$$M \times 100 \equiv \frac{2.14}{107} \times 1000$$

$M_{FeCl_3} = 0.2$

$N_{FeCl_3} = 0.2 \times 3$ (valency factor = 3)

$= 0.6$ N

56. (4) $M_1 = 1.0$ M, $M_2 = 0.25$ M

Let V_1 and V_2 are volumes required.

$(1.0 \times V_1 + 0.25 \times V_2) = 0.75\,(V_1 + V_2)$

$\Rightarrow 0.25V_1 = 0.5V_2, \Rightarrow V_1 : V_2 = 2 : 1$

57. (2)

$$X_{H_2SO_4} = \frac{100 \times 0.9}{100 \times 0.9 + 100 \times 1} = \frac{90}{190} = 0.4736$$

% mass of H_2SO_4 = 47.36%

58. (1) Dibasic acid ≡ NaOH

12.5 mL   10 mL × 0.1 N = 1 mEq

Strength of dibasic acid = $6\ \text{g L}^{-1}$

mEq of acid = mEq of NaOH

$12.5 \times N = 1$ mEq

$$\frac{12.5 \times 6 \times 1000}{\frac{Mw}{2} \times 1000} = 1$$

$\therefore$ Mw (acid) = 150

59. (2) $55.5\ \text{g CaCl}_2 \equiv 50\ \text{g CaCO}_3$

$55.5\ \text{mg CaCl}_2 \equiv 50 \times 10^{-3}\ \text{g CaCO}_3$

$47.5\ \text{g MgCl}_2 \equiv 50\ \text{g CaCO}_3$

$47.5\ \text{mg MgCl}_2 \equiv 50 \times 10^{-3}\ \text{g CaCO}_3$

Total $\text{CaCO}_3 = (50 + 50) \times 10^{-3} = 10^{-2}\ \text{g L}^{-1}$

$$\text{ppm} = \frac{10^{-2}}{1000\ \text{mL}} \times 10^{6}\text{mL} = 10$$

60. (3) 10 mL of 0.2 N HCl + 30 mL of 0.1N HCl ≡ 40 mL of NaOH (≡ 0.61 g organic acid)

mEq of HCl ≡ mEq of NaOH ≡ mEq of organic acid

$$10 \times 0.2 + 30 \times 0.1 \equiv \frac{0.61}{E} \times 1000$$

$$5 = \frac{0.61 \times 1000}{E}$$

$$E = \frac{610}{5} = 122$$

Multiple Correct Answers Type

1. (1, 2) Self explanatory.

2. (2, 3)

2. ⇒ 5 cm (not cms)
3. ⇒ 5 joules (not Joules)

3. (4)

1. Not applicable if the elements exists in different isotopes which may be involved in the formation of compound.
2. At 1 atm, 25°C molar volume = 22.7 L
3. $Mw = 2 \times \text{VD}$
4. Due to existence of isotopes.

4. (1, 2, 3, 4)

1. Valency factor = 6 $\left[\overset{+2\times3}{\text{Ca}_3}\ \overset{-3\times2}{(\text{PO}_4)_2}\right]$
2. Valency factor = 3 $\left[\overset{+1\times3}{\text{Na}_3}\ \overset{-3}{(\text{PO}_4)}\right]$
3. Valency factor = 2 $\left[\overset{+1\times2}{\text{K}_2}\ \overset{-2}{\text{SO}_4}\right]$
4. Valency factor = 8

$$\left[\overset{+1\times2}{\text{K}_2}\ \overset{-2}{\text{SO}_4}\ \overset{+3\times2}{\text{Al}_2}\ \overset{-2\times3}{(\text{SO}_4)_3}\right]$$

5. (3, 4)

(1) and (2) are compound. (3) and (4) are mixture.

6. (1, 4)

1. Number of of O_2 atoms $= \dfrac{16}{32} \times 2 \times N_A = 1 \times N_A$
2. Number of of O_3 atoms $= \dfrac{16}{48} \times 3 \times N_A = 1 \times N_A$
3. **i.** Number of of O_2 molecules $= \dfrac{16}{32} \times N_A = \dfrac{1}{2} N_A$

   ii. Number of of O_2 molecules $= \dfrac{16}{48} \times N_A = \dfrac{1}{3} N_A$

   (4) is correct.

7. (1, 2, 3, 4)

1. Moles of $O_2 = \dfrac{1.6}{32} = 0.05$
2. Molecules of $O_2 = 0.05 \times 6.023 \times 10^{23} = 3.011 \times 10^{22}$
3. Volume of O_2 at STP $= 0.05 \times 22.4 = 1.12$ L
4. V_{O_2} at SATP $= 0.05 \times 24.4 = 1.22$ L

8. (1, 2, 3, 4) Two

9. (1, 2, 3) Three

10. (1, 2, 3, 4) All correct

11. (1, 2, 3, 4) All correct

12. (2, 3, 4) Self explanatory

13. (3, 4) (3) ⇒ isotopes

(4) ⇒ C-12

14. (1, 2, 4) Self explanatory.

15. (1, 2) Self explanatory.

16. (2, 3)

$$n_{H_2} = \frac{64}{2} = 32\ \text{mol}$$

$$n_{O_2} = \frac{64}{32} = 2\ \text{mol}$$

1 mol of O_2 requires = 2 mol of H_2

2 mol of O_2 requires = 4 mol g H_2

Since H_2 is present in excess, therefore, O_2 is the limiting reagent.

1. Wrong.
2. So, O_2 is the limiting reagent
3. 2 mol of O_2 = 4 moles of $H_2O = 4 \times 18 = 72$ g H_2O

   moles of H_2 left $= 32 - 4 = 28$ mol $= 28 \times 2 = 56$ g H_2

   Mixture contains = (72 g H_2O + 56 g H_2)
4. Wrong.

17. (2, 3, 4) $n_{P_4} = \dfrac{1.24}{31 \times 4} = 0.01\ \text{mol}$, $n_{O_2} = \dfrac{8}{32} = 0.25$ moles

In reaction (i), moles of O_2 required

$$= (0.01\ \text{mol P}_4)\left(\frac{5\ \text{mol O}_2}{\text{mol P}_4}\right)$$

$$= 0.01 \times 5 = 0.05\ \text{mol}$$

Since there is more O_2 present than required

1. Therefore, P_4 is the limiting quantity.
2. Wrong.
3. [Mw P_4O_{10} = 284]

   0.01 mol of P_4 produces = 0.01 mol of P_4O_{10}

$$= (0.01\ \text{mol P}_4)\left(\frac{1\ \text{mol P}_4\text{O}_{10}}{\text{mol P}_4\text{O}_{10}}\right)\left(\frac{284\ \text{g P}_4\text{O}_{10}}{\text{mol P}_4\text{O}_{10}}\right)$$

$$= 0.01 \times 284 = 2.84 \text{ g}$$

Hence, (3) is wrong.

4. [Mw of $P_4O_6 = 220$]

Weight of P_4O_6 produced

$$= (0.01 \text{ mol } P_4)\left(\frac{1 \text{ mol } P_4O_6}{\text{mol } P_4O_6}\right)\left(\frac{220 \text{ g } P_4O_6}{\text{mol } P_4O_6}\right)$$

$$= 0.01 \times 220 = 2.2 \text{ g}$$

Hence, (4) is wrong

18. **(1, 2, 3)**

(Mw of $CS_2 = 76$, Mw of $Cl_2 = 71$, Mw of $CCl_4 = 154 \text{ g mol}^{-1}$)

Weight of Cl_2 needed

$$= (1.0 \text{g } CS_2)\left(\frac{1 \text{ mol } CS_2}{76 \text{ g } CS_2}\right)\left(\frac{3 \text{ mol } CS_2}{\text{mol } CS_2}\right)\left(\frac{71 \text{ g } Cl_2}{\text{mol } Cl_2}\right)$$

$$= \frac{1 \times 3 \times 71}{76} = 2.8 \text{ g } Cl_2 \text{ needed}$$

Since there is 2.0 g Cl_2 present, Cl_2 is the limiting quantity

1. Weight of Cs_2 used

$$= (2.0 \text{g } Cl_2)\left(\frac{1 \text{ mol } Cl_2}{71 \text{ g } Cl_2}\right)\left(\frac{1 \text{ mol } CS_2}{3 \text{ mol } Cl_2}\right)\left(\frac{76 \text{ g } CS_2}{\text{mol } CS_2}\right)$$

$$= \frac{2 \times 1 \times 1 \times 76}{71 \times 3} = 0.714 \text{ g } CS_2 \text{ used.}$$

2. Weight of CS_2 excess or formed
= (1.0 g CS_2 present) – (0.714 g used)
= 0.286 g CS_2 formed

3. Weight of CCl_4 formed

$$= (2.0 \text{ g } Cl_2)\left(\frac{1 \text{ mol } Cl_2}{71 \text{ g } Cl_2}\right)\left(\frac{1 \text{ mol } CCl_4}{3 \text{ mol } Cl_2}\right)\left(\frac{154 \text{ g } CCl_4}{\text{mol } CCl_4}\right)$$

$$= \frac{2 \times 1 \times 154}{71 \times 3} = 1.45 \text{ g } CCl_4$$

4. Wrong.

19. **(1, 3)**

$$\text{moles of Al} = \frac{108}{27} = 4.0 \text{ mol}$$

$$\text{moles of MnO} = \frac{213}{71} = 3.0 \text{ mol}$$

1. Since 2 mol of Al requires 3 mol of MnO, therefore Al is in excess.
2. Wrong
3. Weight of Al required

$$= (3.0 \text{ mol MnO})\left(\frac{2 \text{ mol Al}}{3 \text{ mol MnO}}\right)\left(\frac{27 \text{g Al}}{\text{mol Al}}\right)$$

$$= \frac{3 \times 2 \times 27}{3} = 54.0 \text{g of Al}$$

4. Weight of Al in excess = (108 – 54) = 54.0 g

20. **(1, 2, 3, 4)**

$$\text{Moles of Li} = \frac{21}{7} = 3.0 \text{ mol}$$

$$\text{Moles of } O_2 = \frac{32}{32} = 3.0 \text{ mol}$$

1. Since $(3.0 \text{ mol Li})\left(\frac{1 \text{ mol } O_2}{4 \text{ mol Li}}\right) = \frac{3}{4} = 0.75 \text{ mol of } O_2$ is required, therefore (1.0 – 0.75) = 0.25 mol of O_2 is in excess. Hence, Li is the limiting reagent

2. Weight of Li_2O formed

$$= (3.0 \text{ mol Li})\left(\frac{1 \text{ mol } Li_2O}{2 \text{ mol Li}}\right)\left(\frac{30 \text{g } Li_2O}{\text{mol } Li_2O}\right)$$

$$= \frac{3 \times 1 \times 30}{2} = 45.0 \text{ g } Li_2O$$

3. $\text{Moles of K} = \frac{3.9}{39} = 0.1 \text{ mol}$

$$\text{Moles of } Cl_2 = \frac{4.26}{71} = 0.06 \text{ mol}$$

Since $\left(\frac{0.1}{2}\right) = 0.05$ mol of Cl_2 is required. Therefore, (0.06 – 0.05) = 0.01 mol of Cl_2 is in excess.

Hence K is the limiting reagent.

4. Weight of KCl formed

$$= (0.1 \text{ mol K})\left(\frac{1 \text{ mol KCl}}{\text{mol K}}\right)\left(\frac{74.5 \text{ g KCl}}{\text{mol KCl}}\right)$$

$$= 0.1 \times 1 \times 74.5 = 7.45 \text{ g of KCl}$$

21. **(1, 2, 3, 4)**

(Mw of $Na_2CO_3 = 106$, Mw of HCl = 36.5, Mw of NaCl = 58.5)

$$\text{Moles of } Na_2CO_3 = \frac{106}{106} = 1.0 \text{ mol}$$

$$\text{Moles of HCl} = \frac{109.5}{36.5} = 3.0 \text{ mol}$$

1. Since for 1 mol of Na_2CO_3, 2 mol of HCl is required. So, HCl is in excess (3 – 2) = 1.0 mol
   Therefore, Na_2CO_3 is the limiting quantity.
2. Weight of NaCl formed

$$= (1.0 \text{ mol } Na_2CO_3)\left(\frac{2 \text{ mol NaCl}}{\text{mol } Na_2CO_3}\right)\left(\frac{58.5 \text{ g NaCl}}{\text{mol NaCl}}\right)$$

$$= 1 \times 2 \times 58.5 = 117.0 \text{ g NaCl}$$

3. 1 mol of Na_2CO_3 = 1 mol of CO_2 = 22.7 L at 1 bar, 273 K
4. 1 mol of Na_2CO_3 = 1 mol of CO_2 = 24.7 L at 1 bar, 298 K

22. **(3, 4)**

(Let 'a' g of X and Y taken)

$$\begin{array}{lccccc} & 2X & + & 3Y & \longrightarrow & X_2Y_3 \\ \text{Initial moles]} \Rightarrow & \frac{a}{36} & & \frac{a}{24} & & \\ \text{Final moles]} \Rightarrow & - & & - & & \frac{a}{72} \end{array}$$

Since both X and Y are completely consumed, there is no limiting reagent.

Moles of $X_2Y_3 = \frac{a}{72}$,

(Mw of $X_2Y_3 = 2 \times 36 + 24 \times 3 = 144$)

Weight of $X_2Y_3 = \frac{a}{72} \times 144 = 2a = 2 \times$ Weight of X

23. (3, 4)

1. $100 \times 0.1 = 10$ mmol $H^{\oplus}$/150 mL
2. $75 \times 0.1 = 7.5$ mmol $H^{\oplus}$/150 mL
3. $50 \times 0.1 \times 2$ (n factor) $= 10$ mmol/150 mL
4. $100 \times 0.1 = 10$ mmol/150 mL

24. (1, 3, 4) [Mw of KI, $(NH_4)_2SO_4$, $CuSO_4{\cdot}5H_2O$ and Al^{3+}, respectively, are, 166, 132, 250, and 27 g mol^{-1}.]

1. $M = \frac{166 \times 1000}{166 \times 1000} = 1.0$ M
2. $M = \frac{33 \times 1000}{132 \times 200} = 1.25$ M
3. $M = \frac{25 \times 1000}{250 \times 100} = 1.0$ M
4. $M = \frac{27 \times 10^{-3} \times 1000}{27 \times 1} = 1.0$ M

25. (3, 4)

Use, $M = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2}$

1. $M = \frac{5 \times 10 \times 1.07}{58.5} = 0.91$ M ($Cl^{\ominus} = 0.91$ M $= 0.91 \times 35.5 = 32.46$ g)
2. $M = \frac{5 \times 10 \times 1.06}{74.5} = 0.77$ M ($Cl^{\ominus} = 0.77$ M $= 0.77 \times 35.5 = 25.25$ g)
3. $M = \frac{W_2 \times 1000}{Mw_2 \times V_{sol} \text{ (in mL)}}$

   $= \frac{58.5 \times 1000}{58.5 \times 1000} = 1$ M

   ($Cl^{\ominus} = 1$ M $= 1 \times 35.5 = 35.5$ g)
4. $M = \frac{55.5 \times 1000}{111 \times 1000} = 0.5$ M

   $BaCl_2 \longrightarrow Ba^{2+} + 2Cl^{\ominus}$

   $\therefore Cl^{\ominus} = 2 \times M = 2 \times 0.5 = 1$ M $= 1 \times 35.5 = 35.5$ g

26. (1, 2)

Mol of $Cu^{2+} = 1.0$ L $\times 0.1$ M $= 0.1$ mol $Cu^{2+} = 0.1 \times 2$ mol $H^{\oplus}$

1. Weight of CuS $= 0.1 \times 95.5 = 9.55$ g
2. Concentration of $H^{\oplus} = \frac{0.2 \text{ mol}}{1.0\text{L}} = 0.2$ M

(3) and (4) are wrong.

27. (1, 2, 3, 4)

mmoles of HCl $\Rightarrow 20 \times 6 = 120 \Rightarrow 120$ mmol $H^{\oplus}$ + 120 mmol $Cl^{\ominus}$

mmoles of $Ba(OH)_2 \Rightarrow 50 \times 2 = 100 \Rightarrow 100$ mmol Ba^{2+} + 200 mmol $\overset{\ominus}{O}H$

$$H^{\oplus} + \overset{\ominus}{O}H \longrightarrow H_2O$$

Total volume $= 20 + 50 + 30 = 100$ mL

1. $\therefore [\overset{\ominus}{O}H] = \frac{(200 - 120) \text{ mmol}}{100 \text{ mL}} = 0.8$ M
2. $[Cl^{\ominus}] = \frac{120 \text{ mmol}}{100 \text{ mL}} = 1.2$ M
3. $[Ba^{2+}] = \frac{100 \text{ mmol}}{100 \text{ mL}} = 1.0$ M
4. mmoles of $\overset{\ominus}{O}H$ left $= 200 - 120 = 80$ mmol

28. (1, 3)

1. mmoles of $HClO_3 = 100 \times 3 = 300$ mmol

   $= \frac{300}{2}$ mmol of $Ba(ClO_3)_2$

   $= 150$ mmol $= 1.5$ mol
2. Wrong.
3. Weight of $Ba(ClO_3)_2 = 150 \times 10^{-3} \times 304 = 45.6$ g
4. Wrong.

29. (1, 2, 4)

1. Volume of $CCl_4 = 80 \times \frac{80}{100} = 64$ mL
2. Volume of ligroin $= 80 \times \frac{16}{100} = 12.8$ mL
3. Wrong
4. Volume of amyl alcohol $= 80 \times \frac{4}{100} = 3.2$ mL

30. (1, 2, 3, 4)

1. Weight g Al^{3+} in 100 mL of solution $= 100 \times 27$

   $= 2700$ mg $= 2.7$ g

   2 mol Al^{3+} (27×2 g) $\equiv$ 1 mol of $Al_2(SO_4)_3{\cdot}18H_2O$

   $\equiv 666$ g

   2.7 g of $Al^{3+} = \frac{666 \times 2.7}{54} = 33.3$ g
2. Moles of $Cr^{3+} = \frac{26}{52} = 0.5$ mol

   Weight of $CrCl_3{\cdot}6H_2O = 0.5$ mol $Cr^{3+} \times 266.5$ g

   $= 133.25$ g
3. Weight of $NH_4Cl = (100\text{mL})\left(\frac{80 \text{ mg}}{\text{mL}}\right)\left(\frac{10^{-3} \text{ g}}{\text{mg}}\right) = 8.0\text{g}$
4. Weight of $NH_3 = \left(\frac{0.8 \text{ g}}{\text{mL solution}}\right)\left(\frac{20\text{g } NH_3}{100 \text{ g solution}}\right)$

   $= 0.16$ g mL^{-1}

31. **(1, 3, 4)**

$$\mathrm{Ca(NO_3)_2 + Na_2C_2O_4 \longrightarrow CaC_2O_4\downarrow + 2NaNO_3}$$

$Ca(NO_3)_2$	$Na_2C_2O_4$	CaC_2O_4	$NaNO_3$
100 × 0.06 = 6 mmol	50 × 0.06 = 3 mmol	3 mmol = 0.003 mol	—

$Na_2C_2O_4$ is the limiting reagent.

$\therefore$ 3 mmol $Na_2C_2O_4 \equiv$ 3 mmol $Ca(NO_3)_2$

$\equiv$ 3 mmol $CaC_2O_4 \equiv$ 6 mmol $NaNO_3$

mmol of $Ca(NO_3)_2$ left = 6 – 3 = 3 mmol = 0.003 mol

$$M_{Ca^{2+}}\text{(left)} = \frac{3\text{ mmol}}{(100+50)\text{ mL}} = \frac{3}{150} = 0.02\text{ M}$$

Hence, option (2) is wrong.

32. **(2, 4)**

100 mL of 1 M H_2SO_4 + 100 mL (98%, d = 0.1) H_2SO_4

$$\Rightarrow 100 \times 1\text{ M} + 100\text{ mL} \times \left(\frac{98 \times 10 \times 0.1}{98}\right)$$

$$\Rightarrow 100 \times 1\text{ M} + 100 \times 1\ M$$

$$\therefore [H_2SO_4] = \frac{100 \times 1 + 100 \times 1}{200\text{ mL}} = 1\text{ M} = 98\text{ g/1000 mL}$$

$$\text{Mass of } H_2SO_4 = \frac{98\text{ g} \times 200\text{ mL}}{1000\text{ mL}} = 19.6\text{ g}$$

Concentration of each component becomes half of the initial value.

33. **(1, 4)**

$$1\text{ mol } Cl_2 \equiv 2\text{ mol KOH} \equiv 1\text{ mol KClO} \equiv \frac{1}{3}\text{ mol } KClO_3 \equiv \frac{1}{4}\text{ mol } KClO_4$$

$$\text{Moles of } KClO_4 = \frac{277}{138.5} = 2$$

$$\left[\begin{array}{l}\text{Moles of } Cl_2 = 2 \times 4 = 8\\ \text{mass of } Cl_2 = 8 \times 71 = 568\text{ g}\end{array}\right]$$

Moles of KOH = 2 × 8 = 16

$$V_{KOH} = \frac{16}{1.5} = 10.67\text{ L}$$

34. **(1, 2, 3)**

KNO_3 +	HCl +	H_2SO_4
(100 × 0.1 = 10 mmol)	(400 × 0.2 = 80 mmol)	(500 × 0.3 = 150 mmol)

Total volume = 100 + 400 + 500 = 1000 mL

$$M_{K^\oplus} = \frac{10}{1000} = 0.01\text{ M}$$

$$M_{SO_4^{-2}} = \frac{150}{1000} = 0.15\text{ M}$$

$$M_{H^\oplus} = \frac{80 + 2 \times 150}{1000} = 0.38\text{ M}$$

$$M_{NO_3^\ominus} = \frac{10}{1000} = 0.01\text{ M}$$

$$M_{Cl^\ominus} = \frac{80}{1000} = 0.08\text{ M}$$

35. **(1, 3)**

	Silica	H_2O	Impurities
% in original clay] ⇒	40	19	100 – (40 + 19) = 41
% after partial drying] ⇒	a	10	100 – (a + 10) = 90 – a

On heating, only water evaporates from clay, whereas silica and impurities are left as it is. Therefore, % ratio of silica and impurities remains unchanged, i.e.,

$$\frac{40}{a} = \frac{41}{90-a},\ \therefore\ a = 44.4\%$$

% of impurities after partial drying = $(90 - a) = (90 - 44.4)$ = 45.6%

Mass of H_2O evaporated = (19 – 10) = 9 g

36. **(3, 4)**

Equal number of molecules are present when moles are same. For the same mass the molecular weight has to be same.

Hence *Mw* of N_2 = *Mw* of CO = 28 g

Mw of N_2O = *Mw* of CO_2 = 44 g

Linked Comprehension Type

1. **(2)** $NH_2CONH_2 + 2HNO_2 \longrightarrow CO_2\uparrow + 2N_2\uparrow + 3H_2O(l)$

$$\text{mmoles} = \frac{0.3 \times 10^3}{60} = 5$$

	NH_2CONH_2	$2HNO_2$	CO_2	$2N_2$	$3H_2O$
Initial	5	10 (0.2 M)	—	—	—
Final	—	—	5	10	15

V_{H_2O} at room temperature = 0 (since it is liquid).

V_{CO_2} is absorbed by KOH or NaOH.

$\therefore$ millimoles of gases (i.e., N_2) = 10

V at RTP = 24400 × 10 × 10^{-3} mL = 244 mL

2. **(3)** millimoles of HNO_2 = 10 = 0.2 M × V_{HNO_2} (mL)

V_{HNO_2} = 50 mL

3. **(1)** Factor label method: (*Mw* of $NaClO_4$ = 122.5, *Mw* of $NaClO_3$ = 106.5 g mol^{-1})

$$x\text{ g of } Cl_2 = \left(\frac{122.5\text{ g } NaClO_4}{122.5\text{ g } NaClO_4 \text{ per mol of } NaClO_3}\right)\left(\frac{4\text{ mol } NaClO_3}{3\text{ mol } NaClO_4}\right)\left(\frac{3\text{ mol NaClO}}{1\text{ mol } NaClO_3}\right)\left(\frac{1\text{ mol } Cl_2}{1\text{ mol NaClO}}\right)\left(\frac{71.0\text{ g } Cl_2}{1\text{ mol } Cl_2}\right)$$

$$= \frac{\cancel{122.5}}{\cancel{122.5}} \times \frac{4}{\cancel{3}} \times \frac{\cancel{3}}{1} \times \frac{1}{1} \times \frac{71.0}{1} = 284.0\text{ g}$$

Mole method:

$n(NaClO) = n(Cl_2)$,

$$n(NaClO_3) = \frac{1}{3}n(NaClO) = \frac{1}{3}n(Cl_2)$$

$$n(\text{NaClO}_4) = \frac{3}{4}n(\text{NaClO}_3) = \frac{3}{4} \times \frac{1}{3}n(\text{Cl}_2) = \frac{1}{4}n(\text{Cl}_2)$$

$$n(\text{NaClO}_4) = \frac{122.5 \text{ g NaClO}_4}{122.5 \text{ of NaClO}_4 / \text{mol NaClO}_4}$$

$= 1.0 \text{ mol}\cdot\text{NaClO}_4$

$n(\text{Cl}_2) = 4 \times 1.0 = 4 \text{ mol}\cdot\text{Cl}_2$

Mass of $(\text{Cl}_2) = 4 \times 71.0 \text{ g} = 284.0 \text{ g Cl}_2$

4. (2) $$x \text{ g Cl}_2 = \left(\frac{106.5 \text{ g NaClO}_3}{106.5 \cdot \text{g NaClO}_3 \text{ per mol NaClO}_3}\right)\left(\frac{3 \text{ mol NaClO}}{1 \text{ mol NaClO}_3}\right)$$

$$\left(\frac{1 \text{ mol Cl}_2}{1 \text{ mol NaClO}}\right)\left(\frac{71.0 \text{ g Cl}_2}{1 \text{ mol Cl}_2}\right)$$

$$= \frac{106.5}{106.5} \times \frac{3}{1} \times \frac{1}{1} \times \frac{17.0}{1} = 213.0 \text{ g Cl}_2$$

5. (4) (Refer to Illustration 1.78)

118% oleum means 100 g of oleum requires 18 g of H_2O to form 118 g of H_2SO_4.

$$\underset{\substack{1 \text{ mol} \\ (80\text{g})}}{SO_3} + \underset{\substack{1 \text{ mol} \\ (18 \text{ g})}}{H_2O} \longrightarrow H_2SO_4$$

$\therefore$ % of free $SO_3 = \frac{18}{18} \times 80 = 80\%$

6. (2) % of free $SO_3 = 20\%$

i.e., 20 g SO_3 is present in 100 g oleum.

$\because$ 80 g SO_3 requires 18 g H_2O

20 g·SO_3 requires $= \frac{18}{80} \times 20 = 4.5$ g H_2O

$\therefore$ % labelling of oleum = 100 + 4.5 = 104.5%

7. (4) 147% oleum sample implies 100 g oleum sample on addition of 47 g of H_2O will form 147 g H_2SO_4.

Equivalent of $H_2SO_4 = \frac{147}{49} = 3 = 3 \times 10^3$ mEq

$\therefore$ mEq of H_2SO_4 = mEq of NaOH

$3 \times 10^3 = 500 \text{ mL} \times x \times 1$

$x = \frac{3000}{500} = 6$ M

8. (1) *Mw* of $K_2[PtCl_4] = 2 \times 39 + 195 + 4 \times 35.5 = 415$ g, *Mw* of $NH_3 = 17$ g

Mol of $K_2[PtCl_4] = \frac{83.0}{415} = 0.2$ mol (limiting reagent)

Mol of $NH_3 = \frac{83}{17} = 4.88$ mol (excess)

9. (2) Mol of $K_2[PtCl_4]$ consumed = 0.2 mol

= mol of cisplatin

NH_3 consumed = 2 × 0.2 = 0.4 mol.

10. (4) Excess of NH_3 unreacted = 4.88 – 0.4 = 4.48 mol

11. (1) Weight of Na_2SO_4 = (100 g NaCl)

$$\left(\frac{90.0 \text{ g NaCl}}{100 \text{ g mixture}}\right)\left(\frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}}\right)$$

$$\left(\frac{1 \text{ mol Na}_2\text{SO}_4}{2 \text{ mol NaCl}}\right)\left(\frac{142 \text{ g Na}_2\text{SO}_4}{\text{mol Na}_2\text{SO}_4}\right)$$

$$= \frac{100 \times 90 \times 1 \times 1 \times 142}{100 \times 58.5 \times 2}$$

$= 109.79 \approx 109.8$ g

12. (4) Weight of Na_2SO_4 = (109.8 g Na_2SO_4) × $\left(\frac{100 \text{ g new mixture}}{80.0 \text{ g Na}_2\text{SO}_4}\right)$

$$= \frac{109.8 \times 100}{80}$$

= 137.25 g mixture

Matrix Match Type

1. (a → q) 2 mol $NH_4^{\oplus} \equiv 1$ mol of $(NH_4)_2CO_3 = 96$ g

0.4 mol $NH_4^{\oplus} = \frac{96 \times 0.4}{2} = 19.2$ g

(b → r) 8 mol H atoms ≡ 1 mol $(NH_4)_2CO_3 = 96$ g

1 mol H atoms (6.02×10^{23} H atoms)

$= \frac{96}{8} = 12.0$ g

(c → s) $$\underset{1\text{mol}}{(NH_4)_2CO_3} + 2HCl \longrightarrow 2NH_4Cl + \underset{1 \text{ mol}}{CO_2} + H_2O$$

1 mol of $CO_2 \equiv 1$ mol of $(NH_4)_2CO_3 = 96$ g

3 mol of $CO_2 \equiv 96 \times 3 = 288.0$ g

(d → p) 100 mL × 0.2 M = 20 mmol $(NH_4)_2$ CO_3

$= 20 \times 10^{-3} \times 93 = 1.92$ g

2. (a → q) **i.** Moles of $CaCl_2 = \frac{11.1}{111} = 0.1$ mol $CaCl_2$

$= 0.1$ mol Ca^{2+}

$+ 0.2$ mol $Cl^{\ominus}$

ii. Moles of NaCl $= \frac{29.25}{58.5} = 0.5$ mol NaCl

$= 0.5$ mol $Na^{\oplus}$

$+ 0.5$ mol $Cl^{\ominus}$

Adding (i) and (ii), we get

0.1 mol Ca^{2+} + 0.5 mol $Na^{\oplus}$ + 0.7 mol $Cl^{\ominus}$

$\therefore$ $[Ca^{2+}] = \frac{0.1}{100} = 0.001$ M

$[Na^{\oplus}] = \frac{0.5}{100} = 0.005$ M

$[Cl^{\ominus}] = \frac{0.7}{100} = 0.007$ M

(b → p) **i.** NaCl ⇒ 3 × 4 = 12 ⇒ $Na^{\oplus}$ = 12 mol, $Cl^{\ominus}$ = 12 mol

ii. $CaCl_2$ ⇒ 4 × 2 = 8 ⇒ Ca^{2+} = 8 mol, $Cl^{\ominus}$ = 16 mol

Adding (i) and (ii), we get

$12 \text{ mol } Na^{\oplus} + 8 \text{ mol } Ca^{2+} + 28 \text{ mol } Cl^{\ominus}$

$$\therefore [Ca^{2+}] = \frac{8}{10} = 0.8 \text{ M}$$

$$[Na^{\oplus}] = \frac{12}{10} = 1.2 \text{ M}$$

$$[Cl^{\ominus}] = \frac{28}{10} = 2.8 \text{ M}$$

(c → r) **i.** $NaCl = 300 \times 3 = 900 \text{ mmol} \Rightarrow 900 \text{ mmol } Na^{\oplus} + 900 \text{ mmol } Cl^{\ominus}$

ii. $CaCl_2 = 200 \times 4 = 800 \text{ mmol} \Rightarrow 800 \text{ mmol } Ca^{2+} = 1600 \text{ mmol } Cl^{\ominus}$

Adding (i) and (ii), we get

$800 \text{ m mol } Ca^{2+} + 900 \text{ mmol } Na^{\oplus} + 2500 \text{ mmol } Cl^{\ominus}$

Total volume = 300 + 200 = 500 mL

$$\therefore [Ca^{2+}] = \frac{800 \text{ mmol}}{500 \text{ mL}} = 1.6 \text{ M}$$

$$[Na^{\oplus}] = \frac{900 \text{ mmol}}{500 \text{ mL}} = 1.8 \text{ M}$$

$$[Cl^{\ominus}] = \frac{2500 \text{ mmol}}{500 \text{ mL}} = 5 \text{ M}$$

(d → s) **i.** $HCl = 100 \times 2 = 200 \text{ mmol} \Rightarrow 200 \text{ mmol } H^{\oplus} + 200 \text{ mmol } Cl^{\ominus}$

ii. $NaOH = 200 \times 1 = 200 \text{ mmol} \Rightarrow 200 \text{ mmol}$

$Na^{\oplus} + 200 \text{ mmol } \overset{\ominus}{O}H$

Since $H^{\oplus}$ and $\overset{\ominus}{O}H$ react to give H_2O.

$$\underset{200 \text{ mmol}}{H^{\oplus}} + \underset{200 \text{ mmol}}{\overset{\ominus}{O}H} \longrightarrow \underset{200 \text{ mmol}}{H_2O}$$

$Cl^{\ominus} = 200 \text{ mmol}, Na^{\oplus} \Rightarrow 200 \text{ mmol}$

iii. $CaCl_2 \Rightarrow 150 \times 4 = 600 = \text{mmol} \Rightarrow 600 \text{ mmol } Ca^{2+} + 1200 \text{ mmol } Cl^{\ominus}$

iv. Total volume = 200 + 100 + 150 + 50
= 500 mL

v. Total Ca^{2+} = 600 mmol

$$\therefore [Ca^{2+}] = \frac{600}{500} = 1.2 \text{ M}$$

Total $Na^{\oplus}$ = 200 mmol

$$\therefore [Na^{\oplus}] = \frac{200}{500} = 0.4 \text{ M}$$

Total $Cl^{\ominus}$ = 200 + 1200 = 1400 mmol

$$\therefore [Cl^{\ominus}] = \frac{1400}{500} = 2.8 \text{ M}$$

3.

(a → p, q, r) Molarity (M) depends on temperature, dilution, and volume.

(b → q) Molality (m) depends only on dilution.

(c → q) Mole fraction (χ) also depends only on dilution

(d → p, q, r) Normality like molarity depends on all.

4.

(a → r)

$$\underset{\substack{1.0 \text{ g} \\ \frac{1}{2} \text{ mol}}}{2H_2} + \underset{\substack{1.0\text{g} \\ \frac{1}{32} \text{ mol}}}{O_2} \longrightarrow 2H_2O$$

O_2 is the limiting reagent : $1 \text{ mol } O_2 \equiv 2 \text{ mol } H_2O$

$$\Rightarrow \frac{1}{32} \text{ mol } O_2 \equiv \frac{1}{16} \text{ mol } H_2O \equiv \frac{18}{16} \text{ g of } H_2O$$
$$= 1.125 \text{ g}$$

(b → s)

$$\underset{\substack{1.0 \text{ g} \\ \frac{1}{28} \text{ mol}}}{N_2} + \underset{\substack{1.0 \text{ g} \\ \frac{1}{2} \text{ mol}}}{3H_2} \longrightarrow 2NH_3$$

N_2 is the limiting reagent.

$$\therefore \frac{1}{28} \text{ mol } N_2 \equiv \frac{1}{14} \text{ mol } NH_3 \equiv \frac{1}{14} \times 17 \text{ g} = 1.214 \text{ g}$$

(c → p)

$$\underset{\substack{1.0 \text{ g} \\ \frac{1}{100} \text{ mol}}}{CaCO_3} \xrightarrow{\text{Ä}} \underset{\frac{1}{100} \text{ mol}}{CaO} + \underset{\frac{1}{100} \text{ mol}}{CO_2}$$

$$\equiv \frac{1}{100} \times 56 \text{ g CaO}$$
$$\equiv 0.56 \text{ g}$$

(d → q)

$$\underset{\substack{1.0 \text{ g} \\ \frac{1}{12} \text{ mol}}}{C} + \underset{\substack{1.0 \text{ g} \\ \frac{1}{2} \text{ mol}}}{2H_2} \longrightarrow CH_4$$

C is the limiting reagent.

$$\therefore \frac{1}{12} \text{ mol } C \equiv \frac{1}{12} \text{ mol } CH_4 \equiv \frac{16}{12} \text{ g} = 1.333 \text{ g}$$

5. (a → p, q, r, t)

p. mEq of NaOH = 200 × 0.5 = 100 mEq ≡ 100 mEq of H_2SO_4

q. $4.9 \text{ g } H_2\overset{+6}{S}O_4 = \frac{4.9}{98} \times 10^3$

= 50 mmol ≡ 100 mEq (n factor = 2)

≡ 200 mmol of O atoms. (1 mol H_2SO_4 ≡ 4 mol O atoms)

r. Highest oxidation state of S = +6

t. Hybridisation = sp^3; geometry and shape ⇒ Tetrahedral

(b → q, r, t)

$$4.9 \text{ g } H_3PO_4 \equiv \frac{4.9}{98} \times 1000 = 50 \text{ mmol}$$

= 50 × 3 (n factor) ≡ 150 mEq

q. 50 mmol of H_3PO_4 ≡ 50 × 4 = 200 mmol of O atoms).
(1 mol H_3PO_4 ≡ 4 mol O atoms)

p. But 150 mEq H_3PO_4 ≠ mEq of NaOH

t. Hybridisation is sp^3, so geometry and shape is tetrahedral.

r. Maximum oxidation state of P = +5

(c → p, q, r, s)

p. $4.9 \text{ g } H_2C_2O_4 \equiv \frac{4.9}{90} \times 1000$

$= 50 \text{ mmol} = 100 \text{ mEq } (n \text{ factor} = 2)$

q. 50 mmoles of $H_2C_2O_4 \equiv 50 \times 4 = 200$ mmoles O atoms (1 mol $H_2C_2O_4$ = 4 mol o atoms)

$\equiv 100$ mEq NaOH

r. Highest oxidation state of C = +4

s. Reacts with oxidising agents such as $MnO_4^{\ominus}$ and $Cr_2O_7^{2-}$.

(d → r, t)

i. $5.3 \text{ g of } Na_2CO_3 = \frac{5.3}{106} \times 1000$

$= 50$ m moles

ii. Na_2CO_3 does not react with NaOH.

r. Highest oxidation states of C = +4

t. CO_3^{2-}, hybridisation is sp^2, so geometry and shape is planar.

v. 1 mol $Na_2CO_3 \equiv 3$ mol O atoms

6. (a → p, s)

p. $$\left[\begin{array}{l} M = \frac{9.8 \times 10 \times 1.8}{98} = 1.8 \\ N = 1.8 \times 2 = 3.6 \end{array}\right.$$

s. $$\left[\begin{array}{l} d = M\left(\frac{Mw_2}{1000} + \frac{1}{m}\right), \\ 1.8 = 1.8\left(\frac{98}{1000} + \frac{1}{m}\right) \Rightarrow m = 1.10 \end{array}\right.$$

(b → p, q, s)

q. $M = \frac{9.8 \times 10 \times 1.2}{98} = 1.2$

p. $N = 1.2 \times 3 = 3.6$

s. $d = M\left(\frac{Mw_2}{1000} + \frac{1}{m}\right),$

$1.8 = 1.8\left(\frac{98}{1000} + \frac{1}{m}\right) \Rightarrow m = 1.10$

(c → p, r)

$1.8N_A$ molecules = 1.8 mol of HCl 500 mL = 1.8 Eq.

$M = \frac{1.8 \times 1000}{500} = 3.6 \text{ M} = 3.6 \text{ N } (n \text{ factor} = 1)$

(d → r)

mEq of base = $250 \times 4 + 250 \times 1.6 \times 2$

$= 1000 + 800$

$= 1800$ mEq

$= 1.8$ Eq

7. (a → p, q, r)

p., r. mol of $KMnO_4 = \frac{15.8}{158} = 0.1$ mol

$= 6.023 \times 10^{22}$ molecules

q. 0.1 mol $KMnO_4$ = 0.4 mol O atoms

$= 0.4 \times 6.023 \times 10^{22}$ atoms

$= 24.092 \times 10^{22}$ atoms of oxygen

(b → p, q, r)

p., r. mol of $H_2C_2O_4 = \frac{9.0}{9.0} = 0.1$ mol

$= 6.023 \times 10^{22}$ molecules

q. 0.1 mol $H_2C_2O_4$ = 0.4 mol O atoms

$= 24.092 \times 10^{22}$ atoms of oxygen

(c → q, s)

mol of $CO_2 = \frac{8.8}{44} = 0.2$ mol

1 mol CO_2 = 2 mol of O atoms

0.2 Mol CO_2 = 0.4 of O atoms

$= 24.092 \times 10^{22}$ atoms of oxygen

(d → s) Mol of CO $= \frac{5.6}{28} = 0.2$ mol

Numerical Value Type

1. (10) Use $M = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2}$

$M_1V_1 = M_2V_2$

$$\frac{90 \times \cancel{10} \times 0.8}{\cancel{46}} \times V = \frac{10 \times \cancel{10} \times 0.9}{\cancel{46}} \times 80$$

$$V = \frac{10 \times 0.9 \times 80}{90 \times 0.8} = 10 \text{ mL}$$

2. (10) Total mEq of acid = $50 \times 1 + 100 \times 0.5 + x \times 5 \times 2$

(n factor)

$= (100 + 10x)$mEq

$= \frac{(100 + 10x)}{100 \text{ mL}} \text{ N}$

N_1V_1 (Acid) = N_1V_1 [$Al_2(CO_3^{2-})_3$] (Total charge = 6)

(n = 6)

$$\therefore \frac{(100 + 10x)}{100 \text{ mL}} \text{ N} \times 100 \text{ mL} = 10 \text{ mL} \times \frac{1}{3} \times 6$$

$(100 + 10x) = 200$

$\therefore x = 10$ mL

3. (2) $M_1V_1 = N_2V_2$ (Atomic weight of Co = 58.93 g)

$$\frac{100 \text{ mg}}{\cancel{58.93 \text{ mg}}} \times V_1 = \frac{20 \text{ mg}}{\cancel{58.93 \text{ mg}}} \times 10 \text{ mL}$$

$$V_1 = \frac{20 \times 10}{100} = 2 \text{ mL}$$

4. (9) $M = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2} = \frac{30 \times 10 \times 1.095}{36.5} = 9 \text{ M}$

5. (5) The concentration is reduced to 1/5th, without any change in the number of g of solute, hence the volume must increase five fold. Dilute it to 5.0 times its former volume.

6. (8) $\text{Weight of NaOH} = \left(\dfrac{92\text{ g}}{100\text{ g solution}}\right)$ (100 g solution)

$= 92\text{ g NaOH}$

$\text{Weight of H}_2\text{O} = 100 - 92 = 8.0\text{ g H}_2\text{O}$

7. (7) $HCO_3^{\ominus} \longrightarrow CO_2$

Moles $HCO_3^{\ominus}$

$= \dfrac{6.1\text{ g}}{61} \times \dfrac{20.8}{100} = 0.0286\text{ moles of }CO_2$

1 mol CO_2 at 1 atm, and 25°C = 24.4 L

0.0308 mol $CO_2 = 24.4 \times 0.0286 = 0.697 \approx 0.7$ L

$V_{CO2} = 0.7 \times 10 = 7$ L

8. (5) $V_{New} = (V + 1000)$ mL

Number of moles of salt remains same.

$\therefore (V + 1000) \times 1.02 = 1.025 \times 1000$

$V = 4.9\text{ mL} \approx 5\text{ mL}$

9. (3) Total weight = 19.6 g

a. 2.8 g of molecules, $d = 0.765\text{ g L}^{-1}$

$\text{Volume} = \dfrac{\text{Mass}}{d} = \dfrac{2.8}{0.75}\text{ L at STP}$

1 mol ≡ 22.4 L at STP

$\text{moles} = \dfrac{2.8}{0.75} \times \dfrac{1}{22.4}$

$\text{Molecules} = \dfrac{2.8}{0.75} \times \dfrac{1}{22.4} \times 6 \times 10^{23} = 1 \times 10^{23}$

b. 11.2 g molecules, $d = 3\text{ g L}^{-1}$

Molecules = 1×10^{23}

c. 5.6 g molecules, $d = 1.5\text{ g L}^{-1}$

Molecules = 1×10^{23}

Total number of molecules = $3 \times 10^{23} = 3$

Archives

JEE Main

Single Correct Answer Type

1. (3) Mohr's salt is $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Only oxidizable part Fe^{2+} is

$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

Millimoles of $Fe^{2+} = 750 \times 0.06 = 450$

$\text{Moles of }Fe^{2+} = \dfrac{450}{1000} = 0.450\text{ mol}$

$6\text{ mol }Fe^{2+} \equiv 1\text{ mol }Cr_2O_7^{2-}$

$\therefore 0.450\text{ mol }Fe^{2+} = \dfrac{0.450}{6} = 0.075\text{ mol }Cr_2O_7^{2-}$

$= 0.075 \times 294\text{ g} = 22.05\text{ g}$

2. (1) $\text{Molality} = \dfrac{\text{moles of the solute}}{\text{mass of the solvent in kg}}$

$\text{Moles of urea }(n_{\text{urea}}) = \dfrac{0.0100\text{ g}}{60\text{ g mol}^{-1}}$

Mass of 1000 mL of solution = volume × density

$= 300\text{ mL} \times \dfrac{1\text{ g}}{\text{mL}}$ $[\because\ 1\text{dm}^3 = 1000\text{ mL}]$

$= 300\text{ g}$

Mass of solvent $= 300\text{ g} - 0.0100\text{ g}$

$= 299.9\text{ g} = 0.2999\text{ kg}$

$\text{Molality} = \dfrac{0.0100}{60 \times 0.2999} = 5.55 \times 10^{-4}\text{ mol kg}^{-1}$

3. (4) Total mass of solution = 1000 g water + 120 g urea

= 1120 g

Density of solution = 1.15 g/mL

$\text{Thus, volume of solution} = \dfrac{\text{mass}}{\text{density}} = \dfrac{1120\text{ g}}{1.15\text{ g/mL}}$

$= 973.91\text{ mL} = 0.974\text{ L}$

$\text{Moles of solute} = \dfrac{120}{60} = 2\text{ mol}$

$\text{Molarity} = \dfrac{\text{moles of solute}}{\text{volume (L) of solution}} = \dfrac{2\text{ mol}}{0.974\text{ L}} = 2.05\text{ mol L}^{-1}$

4. (1) The molarity of a resulting solution is given by

$M = \dfrac{M_1V_1 + M_2V_2}{V_1 + V_2} = \dfrac{750 \times 0.5 + 250 \times 2}{750 + 250} = \dfrac{875}{1000} = 0.875\text{ M}$

5. (4) 18 g H_2O contains 2 g H.

$\therefore$ 0.72 g H_2O contains 0.08 g H

44 g CO_2 contains 12 g C.

$\therefore$ 3.08 g CO_2 contains 0.84 g C.

$\therefore\ C : H = \dfrac{0.84}{12} : \dfrac{0.08}{1} = 0.07 : 0.08 = 7 : 8$

$\therefore$ Empirical formula = C_7H_8

6. (3) The number of moles is given by

$N = \dfrac{\text{weight }(W)}{\text{molecular weight (M)}}$

Thus, ratio of moles of O_2 and N_2 is given by

$$\frac{n_{O_2}}{n_{N_2}} = \left(\frac{\dfrac{W_{O_2}}{M_{O_2}}}{\dfrac{W_{N_2}}{M_{N_2}}}\right) = \left(\frac{W_{O_2}}{W_{N_2}}\right)\left(\frac{M_{N_2}}{M_{O_2}}\right) = \left(\frac{1}{4}\right) \times \left(\frac{28}{32}\right) = \frac{7}{32}$$

Hence, ratio of n_{O_2} and n_{N_2} is 7 : 32

7. (3) Volume of N_2 in air = 375 × 0.8 = 300 ml

Volume of O_2 in air = 375 × 0.2 = 75 ml

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$

15 ml $\quad 15\left(x + \dfrac{y}{4}\right)$

0 $\quad$ 0 $\quad$ $15x$ $\quad$ —

After combustion, total volume

$330 = V_{N_2} + V_{\infty_2}$

$330 = 300 + 15x$

Volume of O_2 used

$15\left(x + \dfrac{y}{4}\right) = 75$

$x + \dfrac{y}{4} = 5$

$y = 12$

So hydrocarbon is C_2H_{12}.
None of the option matches it, therefore it is another alternative method.

Alternatively

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$

15	$15\left(x+\frac{y}{4}\right)$		
0	0	$15x$	—

Volume of O_2 used

$$15\left(x+\frac{y}{4}\right) = 75$$

$$x+\frac{y}{4} = 5$$

If further information (i.e., 330 ml) is neglected, then option (3) only satisfies the above equation.

8. (1) H is 10% by mass
$\therefore$ H is 7.5 kgs.
It replaced by ^2H weight is doubled i.e., 15 kg
$\therefore$ 7.5 kg increase

9. (2) $M_2CO_3 + 2HCl \longrightarrow 2MCl + H_2O + CO_2$

1 gram	0.01186 mole of CO_2
x gram = 1 mole	1 Mole

$$\Rightarrow x = \frac{1}{0.01186} = 84.3 \text{ g Molar mass}$$

.00186 moles of CO_2 is produced from 1g of M_2CO_3
1 mole of CO_2 in produced from 84.3 g of M_2CO_3 which is equal to 1 mole of M_2CO_3 i.e. its molar mass.

10. (3)

Element	C	:	H		
Mass ratio	6	:	1		
Mole ratio	6/12	:	1	$\Rightarrow$	= 1 : 2

So C_XH_Y have empirical formula :CH_2

For burning a CH_2 limit; oxygen required is $\frac{3}{2}$ mol

$$CH_2 + \frac{3}{2}O_2 \longrightarrow CO_2 + H_2O$$

Empirical formula is $2 \times (CH_2O_{3/2}) \Rightarrow C_2H_4O_3$.

JEE Advanced

Single Correct Answer Type

1. (2) The atomic mass of iron is

$$= \frac{(5\times 54)+(90\times 56)+(5\times 57)}{100} = 55.95$$

2. (3) $V_{sol} = \dfrac{(120+1000)}{1.15}$ mL

$$M = \frac{W_2 \times 1000}{Mw_2 \times V_{sol}} = \frac{120\times 1000}{60\times 1120/1.15} = \frac{2\times 115}{112} = 2.05 \text{ M}$$

3. (1) For a damped pendulum $A = A_0e^{-bt/2m}$

For the given circuit, $A = A_0\,e^{-(R/2L)t}$

L plays the same role as m.

$\because$ $L_1 > L_2$ so with L_1 in the circuit energy dissipation in R will be slower compared to L_2 present in the circuit.

4. (4) 2 mole of $C_8H_7SO_3Na$ = 1 mole of Ca^{+2}

2×206 g $C_8H_7SO_3Na$ = 1 mole of Ca^{+2}

1g $C_8H_7SO_3Na = \dfrac{1}{412}$

Numerical Value Type

1. (3) $Be_nAl_2Si_6O_{18}$
$(2n) + (3\times 2) + (4\times 6) + (-2\times 18) = 0$
or $2n + 30 - 36 = 0$
or $2n = 6$
or $n = 3$

2. (3) A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL and 25.0 mL. The number of significant figures in the average titre value is 3. This is according to the rules of significant figures.

If two or more numbers having different precision are to be added or subtracted, the answer should be taken as the number of decimal places in the number having less decimal places.

3. (7) Density = 10.5 g cc^{-1}
This means 10.5 g silver is present in 1 cm^3.

$\dfrac{10.5}{108}$ mol silver is present in 1 cm^3.

$\dfrac{10.5}{108}$ N silver atoms present in 1 cm^3.

$\sqrt[3]{\dfrac{10.5}{108}N}$ silver atoms present in 1 cm

$\left(\sqrt[3]{\dfrac{10.5}{108}N}\right)^{1/2}$ silver atoms present is 1 cm^2.

10^{-12} m^2 is equal to 10^{-8} cm^2.

$\left(\sqrt[3]{\dfrac{10.5}{108}N}\right)^{1/2} \times 10^{-8}$ silver atoms present in 10^{-12} m^2.

On solving, we get $1.5\times 10^{-7} = Y \times 10^{-x}$
$\therefore x = 7$

4. (2) O, Cl, F, N, P, Sn, Tl, Na, Ti
Na shows only +1.
F shows only −1.

5. (8) Using the formula

$$M = \frac{\%\text{ by mass} \times 10 \times d_{solution}}{Mw_2}$$

$$= \frac{29.2\times 10\times 1.25}{36.5}$$

$\therefore$ $M_1V_1 = M_2V_2$

$$\frac{29.2\times 10\times 1.25}{36.5} \times V_1 = 0.4\times 200 \text{ mL}$$

$10 \times V_1 = 0.4 \times 200$ mL

∴ $V_1 = 8$ mL

(4) $R = k \times N_A = 1.380 \times 10^{-23} \times 6.023 \times 10^{23}$

$= 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

Number of significant digits is 4.

(8) Let us consider, volume of solution = 1 litre = 1000 mL

Weight of solvent = 0.4 × 1000 = 400 g

Weight of solute = 80 g;

Number of moles of solute = 3.2 moles

$$\text{Molality of solution} = (\text{m}) = \frac{w_2 \times 1000}{Mw_2 \times w_1}$$

$$= \frac{n_2 \times 1000}{w_1}$$

$$= \frac{3.2 \times 1000}{400} = 8$$

(9)

$$\frac{\chi_2}{\chi_1} = \frac{0.1}{0.9} = \frac{1}{9}$$

$$W_{\text{soln}} = \text{d}_{\text{soln}} \times V_{\text{soln}}$$

$$= 2V_{\text{soln}}$$

Since $M = m$

$$\therefore \frac{n_2}{V_{\text{soln}}} = \frac{n_2}{W_1}$$

$$\therefore W_1 = V_{\text{soln}} = \frac{W_{\text{soln}}}{2}$$

$$2W_1 = W_{\text{soln}} = W_2 + W_1$$

$$\Rightarrow W_2 = W_1$$

$$\therefore \frac{\chi_2}{\chi_1} = \frac{n_2}{n_1} = \frac{W_2 / Mw_2}{W_1 / Mw_1}$$

$$\frac{1}{9} = \frac{Mw_1}{Mw_2}$$

$$\therefore \frac{Mw_2}{Mw_1} = 9$$

Alternatively,

When $M = m$

$$\frac{\chi_2}{\chi_1} \propto \frac{Mw_1}{Mw_2}$$

Chapter 2

Concept Application Exercises

Exercise 2.1

Subjective Type

1. In reaction (a), Zn donates electrons to O to give zinc and oxide ions. Therefore, Zn acts as a reducing agent while oxygen acts as an oxidising agent.

   In reaction (b), Zn transfers its electrons to $H^{\oplus}$, and therefore, zinc acts as a reducing agent and $H^{\oplus}$ acts as an oxidising agent.

2. For neutral molecule, sum of oxidation number of all the atoms is equal to zero and for a charged species equals to the charge on the ion.

   In H_2S, the oxidation number of H is +1,

   $$H_2S = 2 + x = 0$$
   $$x = -2$$

   Oxidation number of S = −2

   In H_2SO_4, the oxidation number of H is +1, for O it is

   $$H_2SO_4 = 2 + x - 8 = 0$$
   $$x = +6$$

   Oxidation number of S is +6.

   In $S_2O_4^{2-}$, oxidation number of O is −2,

   $S_2O_4^{2-}$: $2x - 8 = -2$

   $$x = 3$$

   ∴ Oxidation number of S is +3.

   In $S_2O_8^{2-}$, we have one peroxide bond; therefore, for two oxygen atoms, oxidation number is −1 and for the other six oxygen atoms, the oxidation number is −2.

   $6 \times (-2) + 2 \times (-1) + 2 \times$ (oxidation number of S) $= -2$

   or oxidation number of S = 6.

   In $HSO_3^{\ominus}$, oxidation number for H is +1 and oxidation number of O is −2,

   1 + (oxidation number of S) + 3(−2) = −1 or oxidation number of S = +4

   It may be noted that sulphur is in different oxidation number states in different compounds. This is true in the next example also in which Cl is in different oxidation states.

3. It is obvious that in HCl the oxidation number for H is +1 and therefore, for Cl it should be −1.

   In HClO, the oxidation number for H is +1 and for O is −2 and therefore, for Cl it should be +1.

   In $ClO_4^{\ominus}$, the oxidation number for O is −2 and therefore, for Cl it should be +7.

   In Ca(OCl)Cl, the oxidation number of Ca is +2 and that of O is −2

   $1 \times 2 + 1 \times (-2) - 2$(oxidation number of Cl) $= 0$

   or oxidation number of Cl is 0.

   It may be mentioned here that one Cl atom exists as chloride ion for which the oxidation number is −1 and the other Cl atom exists as chlorite ion in which the oxidation number of Cl is +1. The oxidation number of Cl in the compound is the average of the oxidation numbers of all the atoms of the element. In this case, the average is zero in agreement with our calculated value.

4. In all these compounds, H has oxidation number +1 and O has oxidation number −2. The values of the oxidation number of carbon in each of the above compounds can be determined using the following general method:

   If the number of hydrogen atoms in the compounds is n_H, the number of oxygen atom is n_0 and the number of carbon atoms in n_C, then we have:

   $n_H(1) + n_O(-2) + n_C$ (oxidation number of carbon) = 0

   or oxidation number of carbon in the compound

   $$= \{n_O(2) - n_H(1)\}/n_C.$$

   The results for different compounds are given in the table below:

Compound	n_H	n_O	n_C	Oxidation number of C $\{n_O \times (2) - n_H\}/n_C$
CH_4	4	0	1	−4
CH_3OH	4	1	1	−2
CH_2O	2	1	1	0
HCOOH	2	2	1	+2
C_2H_4	4	0	2	−2
C_2H_2	2	0	2	−1

5. In Fe_3O_4, each O has oxidation number = −2 and therefore we have:

   4(−2) + 3(oxidation number of Fe) = 0

   or the oxidation number of Fe = 8/3

   Actually Fe_3O_4, known as magnetic oxide of iron, is a stoichiometric mixture of ferrous (FeO) and ferric (Fe_2O_3) oxides and the value 8/3 for the oxidation number is the average of all the Fe atoms in the molecule.

   In the ferriferrocyanide molecule, $Fe_4[Fe(CN)_6]_3$, we have 4 iron atoms with oxidation number +3 and 3 iron atoms with oxidation number +2 and the oxidation number of iron in the molecule is the average of all these atoms equal to 18/7.

   $$7Fe = 4 \times (+3) + 3 \times (+2)$$
   $$7Fe = 18$$
   $$Fe = \frac{18}{7}$$

6. In reaction (a), there is no change in the oxidation number of H and O. Oxidation number of Zn changes from 0 to +2, and therefore, it is oxidised and hence acts as a reductant. The oxidation number of N in nitrite ion is +5 and in ammonium ion it is −3, and therefore, it is reduced and acts as an oxidant.

   In reaction (b) the oxidation number of I changes from 0 to −1. Therefore, it is reduced and acts as an oxidant.

The oxidation number of S in H_2S changes from −2 to 0. Therefore, it is oxidised and hence acts as a reductant.

7. a. H_2S is oxidised because a more electronegative element Cl_2 is added to H. Alternatively, a more electropositive element H has been removed from S. Cl_2 is reduced due to addition of H to it.

b. Al is oxidised because oxygen is added to it. Fe_3O_4 (ferrous ferric oxide) is reduced because oxygen has been removed from it.

c. $2\overset{0}{Na}(s) + \overset{0}{H_2}(g) \longrightarrow 2\overset{0}{Na}\overset{-1}{H}(s)$

$2Na \longrightarrow 2\overset{+1}{Na} + 2e^-$ (oxidation)

$H_2 + 2e^- \longrightarrow 2H^{\ominus}$ (reduction)

Therefore, Na is oxidised and H is reduced.

Alternatively, according to the concept of electronegativity, the more electronegative element H is added to Na, so Na is oxidised and H_2 is reduced.

8. a. $2\overset{+1}{Cu_2}\overset{-2}{O}(s) + \overset{+1}{Cu_2}\overset{-2}{S}(s) \longrightarrow 6\overset{0}{Cu}(s) + \overset{+4-2}{SO_2}$

In the reaction, Cu is reduced from +1 oxidation state to 0 oxidation state and S is oxidised from −2 to +4 state. Thus, it is a redox reaction.

Moreover, Cu_2O helps S in Cu_2S to increase its oxidation number, therefore Cu^{1+} is an oxidant and S in Cu_2S helps Cu both in Cu_2S itself and Cu_2O to decrease its oxidation number; therefore, S in Cu_2S is reductant.

b. In this reaction, compound formed is ionic ($Na^{\oplus}H^{\ominus}$). Two half reactions are

$$2Na(s) \longrightarrow 2Na^{\oplus} + 2e^-$$
$$H_2(g) + 2e^- \longrightarrow 2H^{\ominus}(g)$$

These two reactions show that Na is oxidised and H_2 is reduced. Therefore, complete reaction is a redox change

9. a. $6e^- + 2NO_2^{\ominus} \longrightarrow N_2$ (reduction)

$2x - 8 = -2 \qquad 2x = 0$

$2x = 6$

b. $VO_2^{\ominus} \longrightarrow VO_3^{\ominus} + 2e^-$ (oxidation)

$x - 4 = -1 \qquad x - 6 = -1$

$x = 3 \qquad x = 5$

c. $2e^- + ClO^{\ominus} \longrightarrow Cl^{\ominus}$ (reduction)

$x - 2 = -1 \qquad x = -1$

$x = 1$

d. $2CrO_4^{2-} \longrightarrow Cr_2O_7^{2-}$ (no change in oxidation number number of Cr)

$2x - 16 = -4 \qquad 2x - 14 = -2$

$2x = 12 \qquad 2x = 12$

10.

	Stock notation	Name of the compound
a.	$\overset{+1\times2}{Na_2}\,\overset{+6\times2}{Cr_2}\,\overset{-2\times7}{O_7}$, $Na_2Cr_2(VI)O_7$	Sodium dichromate
b.	$\overset{+7\times2}{Mn_2}\,\overset{-2\times7}{O_7}$, $Mn_2(VII)O_7$	Manganese heptaoxide
c.	$\overset{+5\times2}{V_2}\,\overset{-2\times7}{O_5}$, $V_2(V)O_5$	Vanadium pentaoxide
d.	$\overset{+1\times2}{K_2}\,\overset{+6}{Cr}\,\overset{-2\times4}{O_4}$, $K_2Cr(VI)O_4$	Potassium chromate
e.	$\overset{+3\times2}{Cr_2}\,\overset{-2\times3}{O_3}$, $Cr_2(III)O_3$	Chromium trioxide
f.	$\overset{+2}{Fe}\,\overset{+6}{S}\,\overset{-2\times4}{O_4}$, $Fe(II)SO_4$	Ferrous sulphate
g.	$\overset{+3\times2}{Fe_2}\,\overset{-2\times3}{(SO_4)_3}$, $Fe_2(III)(SO_4)_3$	Ferric sulphate
h.	$\overset{+2}{Cu}\,\overset{-1\times2}{Br_2}$, $Cu(II)Br_2$	Cupric bromide
i.	$\overset{+1\times2}{Cu_2}\,\overset{-1\times2}{Br_2}$, $Cu_2(I)Br_2$	Cuprous bromide

Exercise 2.2

Subjective Type

1.

	a	b	c	d	e
Oxidised	$CN^{\ominus}$	C_6H_5OH	$I^{\ominus}$	$S_2O_3^{2-}$	C
Reduced	$OCl^{\ominus}$	O_3	O_3	Cl_2	ZnO

2. a. −1 b. +7 c. +5 d. +7

3. a. $18H^{\oplus} + 16e^- + 3IO_3^{\ominus} \longrightarrow I_3^{\ominus} + 9H_2O$

$3x - 18 = -3 \qquad 3x = -1$

$3x = 15$

$15 - (-1) = 16e^-$

b. $2H^{\oplus} + e^- + NO_3^{\ominus} \longrightarrow NO_2 + H_2O$

$x - 6 = -1 \qquad x - 4 = 0$

$x = 5 \qquad x = 4$

$5 - 4 = 1e^-$

c. $2H^{\oplus} + e^- + VO^{2+} \longrightarrow V^{3+} + H_2O$

$x - 2 = 2 \qquad x = 3$

$x = 4$

$4 - 3 = 1e^-$

4. a. $Cr_2O_7^{2-} + \cancel{6e^-} + 14H^{\oplus} \longrightarrow 2Cr^{3+} + 7H_2O$

$2I^{\ominus} \longrightarrow I_2 + \cancel{2e^-}\,] \times 3$

$Cr_2O_7^{2-} + 6I^{\ominus} + 14H^{\oplus} \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

Add other ions to both sides, i.e.,

$\text{LHS}\begin{bmatrix}2K^{\oplus}\\8I^{\ominus}\end{bmatrix} \qquad \text{RHS}\begin{bmatrix}2K^{\oplus}\\8I^{\ominus}\end{bmatrix}$

The net redox equation is:

$$K_2Cr_2O_7 + 14HI \longrightarrow 2CrI_3 + 3KI + 3I_2 + 7H_2O$$

b. $\cancel{e^-} + MnO_4^{\ominus} \longrightarrow MnO_4^{2-}] \times 2$

$x - 8 = -1$ $\quad$ $x - 8 = -2$

$x = 7$ $\quad$ $x = 6$

$2\overset{\ominus}{O}H + \cancel{H_2O} + SO_3^{2-} \longrightarrow SO_4^{2-} + \cancel{2e^-} + \cancel{2}H_2O$

$x - 6 = -2$ $\quad$ $x - 8 = -2$

$x = 4$ $\quad$ $x = 6$

$$2MnO_4^{\ominus} + SO_3^{2-} + 2\overset{\ominus}{O}H \longrightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O$$

Add other ions to both sides, i.e., $4K^{\oplus}$, $2Na^{\oplus}$, the net redox equation is

$$2KMnO_4 + Na_2SO_3 + 2KOH \longrightarrow 2K_2MnO_4 + Na_2SO_4 + H_2O$$

c. $Sn^{2+} \longrightarrow Sn^{4+} + \cancel{2e^-}] \times 4$

$8H^{\oplus} + \cancel{8e^-} + IO_4^{\ominus} \longrightarrow I^{\ominus} + 4H_2O$

$x - 8 = -1$ $\quad$ $x = -1$

$x = 7$

$7 - (-1) = 8e^-$

$$4Sn^{2+} + IO_4^{\ominus} + 8H^{\oplus} \longrightarrow 4Sn^{4+} + I^{\ominus} + 4H_2O$$

d. $4\overset{\ominus}{O}H + 2H_2O + Mn^{2+} \longrightarrow MnO_2 + \cancel{2e^-} + 4H_2O$

$x = 2$ $\quad$ $x - 4 = 0$

$x = 4$

$4 - 2 = 2e^-$

$2\cancel{H_2O} + \cancel{2e^-} + H_2O_2 \longrightarrow \cancel{2H_2O} + 2\overset{\ominus}{O}H$

$$2\overset{\ominus}{O}H + Mn^{2+} + H_2O_2 \longrightarrow MnO_2 + 2H_2O$$

e. $14\overset{\ominus}{H} + \cancel{6e^-} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 2H_2O$

$2x - 14 = -2$ $\quad$ $2x = 6$

$2x = 12$

$12 - 6 = 6e^-$

$H_2O_2 \longrightarrow O_2 + 2\overset{\oplus}{H} + \cancel{2e^-}] \times 3$

$$8H^{\oplus} + Cr_2O_7^{2-} + 3H_2O_2 \longrightarrow 2Cr^{3+} + 3O_2 + 7H_2O$$

5. a. Basic medium

$4H_2O + \cancel{3e^-} + MnO_4^{\ominus} \longrightarrow MnO_2 + 2H_2O + 4\overset{\ominus}{O}H] \times 4$

$x - 8 = -1$ $\quad$ $x - 4 = 0$

$x = 7$ $\quad$ $x = 4$

$5\overset{\ominus}{O}H + H_2O + C_2H_5OH \longrightarrow CH_3CO\overset{\ominus}{O} + \cancel{4e^-} + 5H_2O] \times 3$

$2x + 6 - 2 = 0$ $\quad$ $2x + 3 - 4 = -1$

$2x = -4$ $\quad$ $2x = 0$

$$4MnO_4^{\ominus} + 3C_2H_5OH \longrightarrow 4MnO_2 + 3CHCO\overset{\ominus}{O} + \overset{\ominus}{O}H + 4H_2O$$

b. Basic medium

$4\overset{\ominus}{O}H + N_2H_4 \longrightarrow N_2 + \cancel{4e^-} + 4H_2O$

$2x + 4 = 0$ $\quad$ $2x = 0$

$2x = -4$

$\cancel{e^-} + [Fe(CN)_6]^{3-} \longrightarrow [Fe(\overset{-1}{CN}_6)]^{4-}] \times 4$

$$4\overset{\ominus}{O}H + N_2H_4 + 4[Fe(CN)_6]^{3-} \longrightarrow N_2 + 4[Fe(CN)_6]^{4-} + 4H_2O$$

c.

$4H_2O + \cancel{3e^-} + MnO_4^{\ominus} \longrightarrow MnO_2 + 2H_2O + 4\overset{\ominus}{O}H] \times 2$

$x - 8 = -1$ $\quad$ $x - 4 = 0$

$x = 7$ $\quad$ $x = 4$

$2\overset{\ominus}{O}H + H_2O + CN^{\ominus} \longrightarrow CNO^{\ominus} + \cancel{2e^-} + 2H_2O] \times 3$

$x - 3 = -1$ $\quad$ $x - 3 - 2 = -1$

$x = 2$ $\quad$ $x = 4$

$$H_2O + 2MnO_4 + 3CN^{\ominus} \longrightarrow 2MnO_2 + 3CNO^{\ominus} + 2\overset{\ominus}{O}H$$

d. $2NH_3 \longrightarrow N_2 + \cancel{6e^-} + \cancel{6H^{\oplus}}$

$2x + 6 = 0$ $\quad$ $2x = 0$

$2x = -6$

$\cancel{2H^{\oplus}} + \cancel{2e^-} + CuO \longrightarrow Cu + H_2O] \times 3$

$x - 2 = 0$ $\quad$ $x = 0$

$x = 2$

$$2NH_3 + 3CuO \longrightarrow N_2 + 3Cu + 3H_2O$$

e. $2HI \longrightarrow I_2 + \cancel{2e^-} + \cancel{2H^{\oplus}}] \times 3$

$2 + 2x = 0$ $\quad$ $2x = 0$

$\cancel{2} = -2$

$3H^{\oplus} + 3e^- + HNO_3 \longrightarrow NO + 2H_2O] \times 2$

$1 + x - 6 = 0$ $\quad$ $x - 2 = 0$

$x = 5$ $\quad$ $x = 2$

$$6HI + 2HNO_3 \longrightarrow 3I_2 + 2NO + 4H_2O$$

f. $H_2S \longrightarrow S + \cancel{2e^-} + \cancel{2H^{\oplus}}] \times 2$

$2 + x = 0$ $\quad$ $x = 0$

$x = -2$

$\cancel{4H^{\oplus}} + \cancel{4e^-} + SO_2 \longrightarrow S + 2H_2O$

$x - 4 = 0$ $\quad$ $x = 0$

$x = 4$

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

6. a. $\cancel{e^-} + Mn^{3+} \longrightarrow Mn^{2+}$

$x = 3$ $\quad$ $x = 2$

$2H_2O + Mn^{3+} \longrightarrow MnO_2 + \cancel{e^-} + 4H^{\oplus}$

$x = 3$ $\quad$ $x - 4 = 0$

$x = 4$

$$2Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + MnO_2 + 4H^{\oplus}$$

b. $$Mn \longrightarrow Mn^{2+} + \cancel{2e}$$

$x = 0$ $x = 2$

$$2H^{\oplus} + \cancel{e} + NO_3^{\ominus} \longrightarrow NO_2 + H_2O] \times 2$$

$x - 6 = -1$ $x - 4 = 0$

$x = 5$ $x = 4$

$$4H^{\oplus} + 2NO_3^{\ominus} + Mn \longrightarrow Mn^{2+} + 2NO_2 + 2H_2O$$

c. $$F_2^{2+} \longrightarrow Fe^{3+} + \cancel{e}\ ] \times 2$$

$$2H + 2\cancel{e} + H_2O_2 \longrightarrow 2H_2O$$

$$2H^{\oplus} + 2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O$$

d. $$4H^{\oplus} + 3e^- + NO_3^{\ominus} \longrightarrow NO + 2H_2O] \times 4$$

$x - 6 = -1$ $x - 2 = 0$

$x = 5$ $x = 2$

$$2H_2O + Te \longrightarrow TeO_2 + 4\cancel{e} + 4H^{\oplus}] \times 3$$

$x = 0$ $x - 4 = 0$

$x = 4$

$$4H^{\oplus} + 4NO_3^{\ominus} + 3Te \longrightarrow 4NO + 3TeO_2 + 2H_2O$$

7. Basic medium

a. $$4H_2O + 3e^- + CrO_4^{2-} \longrightarrow [Cr(OH)_4]^{\ominus} + 4\overset{\ominus}{O}H$$

$x - 8 = -2$ $x - 4 = -1$

$x = 6$ $x = 3$

b. $$2H_2O + 2e^- + ClO^{\ominus} \longrightarrow Cl^{\ominus} + H_2O + 2\overset{\ominus}{O}H$$

$x - 2 = -1$ $x = -1$

$x = 1$

c. $$6\overset{\ominus}{O}H + \cancel{3H_2O} + Bi^{3+} \longrightarrow BiO_3^{\ominus} + 2e^- + \overset{3}{\cancel{6H_2O}}$$

$x = 3$ $x - 6 = -1$

$x = 5$

8. Basic medium

a. $$\overset{2}{\cancel{4H_2}}O + 4e^- - ClO_4^{\ominus} \longrightarrow ClO_2^{\ominus} + \cancel{2H_2O} + \cancel{4\overset{\ominus}{O}H}$$

$x - 8 = -1$ $x - 4 = -1$

$x = 7$ $x = 3$

$$2\cancel{\overset{\ominus}{O}H} + H_2O_2 \longrightarrow O_2 + \cancel{2e} + \cancel{2H_2O}] \times 2$$

$2 + 2x = 0$ $2x = 0$

$2x = -2$

$$ClO_4^{\ominus} + 2H_2O_2 \longrightarrow ClO_2^{\ominus} + 2O_2 + 2H_2O$$

b.

$$\cancel{\overset{\ominus}{O}H} + H_2O + Fe(OH)_2 \longrightarrow Fe(OH)_3 + e^- + \cancel{H_2O}] \times 3$$

$x - 2 = 0$ $x - 3 = 0$

$x = 2$ $x = 3$

$$4H_2O + 3e^- + CrO_4^{2-} \longrightarrow [Cr(OH)_4]^{\ominus} + 4\overset{\ominus}{O}H$$

$x - 8 = -2$ $x - 4 = -1$

$x = 6$ $x = 3$

$$4H_2O + 3Fe(OH)_2 + CrO_4^{2-} \longrightarrow 3Fe(OH)_3 + [Cr(OH)_4]^{\ominus} + \overset{\ominus}{O}H$$

c. $$4\overset{\ominus}{O}H + N_2H_4 \longrightarrow N_2 + 4\cancel{e} + \cancel{4H_2O}$$

$2x + 4 = 0$ $2x = 0$

$2x = -4$

$$\cancel{2H_2O} + \cancel{2e} + Cu(OH)_2 \longrightarrow Cu + 2H_2O + \cancel{2\overset{\ominus}{O}H}] \times 2$$

$x - 2 = 0$ $x = 0$

$x = 2$

$$N_2H_4 + 2Cu(OH)_2 \longrightarrow N_2 + 2Cu + H_2O$$

d. $$4H_2O + \cancel{3e} + MnO_4^{\ominus} \longrightarrow MnO_2 + \cancel{2H_2O} + 4\overset{\ominus}{O}H] \times 2$$

$x - 8 = -1$ $x - 4 = 0$

$x = 7$ $x = 4$

$$2\overset{\ominus}{O}H + \cancel{H_2O} + IO_3^{\ominus} \longrightarrow IO_4^{\ominus} + \cancel{2e} + 2\cancel{H_2O}] \times 3$$

$x - 6 = -1$ $x - 8 = -1$

$x = 5$ $x = 7$

$$2MnO_4^{\ominus} + 3IO_3^{\ominus} + H_2O \longrightarrow 2MnO_2 + 3IO_4^{\ominus} + 2\overset{\ominus}{O}H$$

9. a. $$Fe^{2+} \longrightarrow Fe^{3+} + \cancel{e}\ ] \times 2$$

$$2H^{\oplus} + 2\cancel{e} + H_2O_2 \longrightarrow 2H_2O$$

$$2Fe^{2+} + H_2O_2 + 2H^{\oplus} \longrightarrow 2Fe^{3+} + 2H_2O$$

b. $$3H_2O + I^{\oplus} \longrightarrow IO_3^{\ominus} + 4e^- + 6H^{\oplus}$$

$x = +1$ $x - 6 = -1$

$x = 5$

Add $Br^{\ominus}$ to both sides.

$$3H_2O + IBr \longrightarrow IO_3^{\ominus} + \cancel{4e} + 6H^{\oplus} + Br^{\ominus}] \times 3$$

$$6H^{\oplus} + \cancel{6e} + BrO_3^{\ominus} \longrightarrow Br^{\ominus} + 3H_2O] \times 2$$

$x - 6 = -1$ $x = -1$

$x = 5$

$$3H_2O + 3IBr + 2BrO_3^{\ominus} \longrightarrow 3IO_3^{\ominus} + 5Br^{\ominus} + 6H^{\oplus}$$

c. $$2I^{\ominus} \longrightarrow I_2 + 2e^-] \times 5$$

$2x = -2$ $2x = 0$

$$12H^{\oplus} + 10e^- + 2IO_3^{\ominus} \longrightarrow I_2 + 6H_2O$$

$2x - 12 = -2$ $2x = 0$

$2x = 10$

$$10\,I^{\ominus} + 2IO_3^{\ominus} + 12H^{\oplus} \longrightarrow 6I_2 + 6H_2O$$

d. Peroxide ion ($O_2^{\ominus}$) undergoes reduction to give $\overset{\ominus}{O}H$ and H_2O undergoes oxidation to give O_2.

$$2H^{\oplus} + 3e^- + O_2^{\ominus} \longrightarrow 2HO^{\ominus}] \times 4$$

$2x = -1$ $2 + 2x = -2$

$2x = -4$

$$2H_2O \longrightarrow O_2 + \cancel{4e^-} + 4H^{\oplus}] \times 3$$

$$4 + 2x = 0 \qquad 2x = 0$$

$$2x = -4$$

$$4O_2^{\ominus} + 6H_2O \longrightarrow 8HO^{\ominus} + 3O_2 + 4H^{\oplus}$$

e. $$3H_2O + 2HS^{\ominus} \longrightarrow S_2O_3^{2-} + 8e^- + 8H^{\oplus}$$

$$2 + 2x = -2 \qquad 2x - 6 = -2$$

$$2x = -4 \qquad 2x = 4$$

$$4H^{\oplus} + 4e^- + 2HSO_3^{\ominus} \longrightarrow S_2O_3^{2-} + 3H_2O] \times 2$$

$$2 + 2x - 12 = -2 \qquad 2x = 2$$

$$2x = 8$$

$$2HS^{\ominus} + 4HSO_3^{\ominus} \longrightarrow 3S_2O_3^{2-} + 3H_2O$$

f. $$[4H_2O + P \longrightarrow H_2PO_4^{\ominus} + 5e^- + 6H^{\oplus}] \times 4$$

$$x = 0 \qquad 2 + x - 8 = -1$$

$$x = 5$$

or

$$16H_2O + P_4 \longrightarrow 4H_2PO_4^{\ominus} + \cancel{20e^-} + 24H^{\oplus}] \times 3$$

$$4H^{\oplus} + \cancel{3e^-} + NO_3^{\ominus} \longrightarrow NO + 2H_2O] \times 20$$

$$x - 6 = -1 \qquad x - 2 = 0$$

$$x = 5 \qquad x = 2$$

$$8H^{\oplus} + 8H_2O + 3P_4 + 20NO_3^{\ominus} \longrightarrow 12H_2PO_4^{\ominus} + 20NO$$

g. Here, As_2S_3 is split into two parts $\overset{+3\times2}{As_2}$ and $\overset{-2\times3}{S_3}$ in which As_2^{6+} is oxidised to H_3AsO_4 and S_3^{-6} is also oxidised to S. Balance both the equations and add them to get the final equation.

$$8H_2O + As_2^{6+} \longrightarrow 2H_3AsO_4 + 4e^- + 10H^{\oplus}$$

$$2x = 6 \qquad 6 + 2x - 16 = 0$$

$$2x = 10$$

$$S_3^{-6} \longrightarrow 3S + 6e^-$$

$$3x = -6 \qquad 3x = 0$$

$$\cancel{8H_2O} + As_2S_3 \longrightarrow 2H_3AsO_4 + 3S + 10H^{\oplus} + \cancel{10e^-} \quad \text{...(i)}$$

$$8H^{\oplus} + \cancel{5e^-} + MnO_4^{\ominus} \longrightarrow Mn^{2+} + \cancel{4H_2O}] \times 2 \quad \text{...(ii)}$$

$$x - 8 = -1 \qquad x = 2$$

$$x = 7$$

$$6H^{\oplus} + As_2S_3 + 2MnO_4^{\ominus} \longrightarrow 2Mn^{2+} + 2H_3AsO_4 + 3S$$

h. Split CrI_3 into two parts $\left(\overset{+3}{Cr} \text{ and } \overset{-1\times3}{I_3}\right)$ in which Cr^{3+} is oxidised to CrO_4^{2-} and I_3^{3-} is also oxidised to $IO_4^{\ominus}$. Balance both the equations in basic medium and add them to get the final equation.

$$8\overset{\ominus}{O}H + \cancel{4H_2O} + Cr^{3+} \longrightarrow CrO_4^{2-} + 3e^- + \cancel{8H_2O}$$

$$x = 3 \qquad x - 8 = -2$$

$$x = 6$$

$$24\overset{\ominus}{O}H + \cancel{12H_2O} + I_3^{-3} \longrightarrow 3IO_4^{\ominus} + 24e^- + \cancel{12H_2O}$$

$$3x = -3 \qquad 3x - 24 = -3$$

$$3x = 21$$

$$32\overset{\ominus}{O}H + CrI_3 \longrightarrow CrO_4^{2-} + 3IO_4^{\ominus} + 16H_2O + \cancel{27e^-}] \times 2$$

$$\cancel{2H_2O} + \cancel{2e^-} + H_2O_2 \longrightarrow 2H_2O + 2\overset{\ominus}{O}H] \times 27$$

$$2 + 2x = 0 \qquad 4 + 2x = 0$$

$$2x = -2 \qquad 2x = -4$$

$$10\overset{\ominus}{O}H + 2CrI_3 + 27H_2O_2 \longrightarrow 2CrO_4^{2-} + 6IO_4^{\ominus} + 32H_2O$$

i. Split Fe_2S_3 into two parts $\left(\overset{+3\times2}{Fe_2}\ \overset{-2\times3}{S_3}\right)$ in which S_3^{6-} undergoes oxidation to S and O_2 undergoes reduction to $\overset{\ominus}{O}H$ in **basic medium.**

$$S_3^{6-} \longrightarrow 3S + \cancel{6e^-}] \times 2$$

$$3x = -6 \qquad 3x = 0$$

$$2H_2O + \cancel{4e^-} + O_2 \longrightarrow 2HO^{\ominus} + 2HO^{\ominus}] \times 3$$

$$2x = 0 \qquad 2 + 2x = -2$$

$$2x = -4$$

$$6H_2O + 2S_3^{6-} + 3O_2 \longrightarrow 6S + 12HO^{\ominus}$$

Add $4Fe^{3+}$ to both sides.

$$6H_2O + 2Fe_2S_3 + 3O_2 \longrightarrow 6S + 4Fe(OH)_3$$

j. $$6H^{\oplus} + \cancel{6e^-} + IO_3^{\ominus} \longrightarrow I^{\ominus} + 3H_2O$$

$$x - 6 = -1 \qquad x = -1$$

$$x = 5$$

$$H_2O + HSO_3^{\ominus} \longrightarrow SO_4^{2-} + \cancel{2e^-} + 3H^{\oplus}] \times 3$$

$$1 + x - 6 = -1 \qquad x - 8 = -2$$

$$x = 4 \qquad x = 6$$

$$IO_3^{\ominus} + 3HSO_3^{\ominus} \longrightarrow I^{\ominus} + 3SO_4^{2-} + 3H^{\oplus}$$

k. $$\cancel{e^-} + Fe^{3+} \longrightarrow Fe^{2+}] \times 4$$

$$2NH_2OH \longrightarrow N_2O + \cancel{4e^-} + H_2O + 4H^{\oplus}$$

$$2x + 4 - 4 + 2 = 0 \qquad 2x - 2 = 0$$

$$2x = -2 \qquad 2x = 2$$

$$4Fe^{+3} + 2NH_2OH \longrightarrow 4Fe^{2+} + N_2O + H_2O + 4H^{\oplus}$$

Objective Type

10. (1)

$$14H^{\oplus} + \cancel{6e^-} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$2x - 14 = -2 \qquad 2x = 6$$

$$2x = 12$$

$$Ni \longrightarrow Ni^{+2} + \cancel{2e^-}] \times 3$$

$$14H^{\oplus} + CrO_7^{2-} + 3Ni \longrightarrow 2Cr^{3+} + 3Ni^{2+} + 7H_2O$$

11. (1) $SO_x^{2-} \longrightarrow 6 - 2x = -2$

$\therefore 2x = 8$

$x = 4$

12. (3) 1. H_2O_2 undergoes oxidation to O_2 and also undergoes reduction to give H_2O (−1 oxidation state to 0 and −2).

2. S^{2-} undergoes only oxidation either to S, SO_2 or SO_4^{2-} in which oxidation number changes from −2 to 0, +4, or +6.

3. SO_2 (oxidation number of S is +4) can undergo oxidation and reduction. S is having highest oxidation state of +6. The element in a molecule having its oxidation state in the middle (i.e., > minimum and < maximum) can be used as oxidant and as reductant both.

4. HNO_2 (oxidation number of N is +3). Highest oxidation state of N is +5. So it can undergo both oxidant and reductant.

13. (2) Oxidation state of S in (a), (b), (c), and (d) are +4, +6, +5/2, and 2, respectively.

14. (2) $14e^- + 2NO_3^{\ominus} \longrightarrow N_2H_4$

$2x - 12 = -2 \qquad 2x + 4 = 0$

$2x = 10 \qquad 2x = -4$

So number of electrons involved for the reduction of 1 mol of $NO_3^{\ominus}$ ion is 7.

15. (3) $H_2PO_2^{-1} = 2 + x - 4 = -1 \Rightarrow x = +1$

16. (4) Cu^{1+} is changing to Cu and Cu^{2+}, i.e., from oxidation number of +1 to 0 and +2.

17. (4) $CN^{\ominus} \longrightarrow CNO^{\ominus} + 2e^-$

$x - 3 = -1 \qquad x - 3 - 2 = -1$

$x = 2 \qquad x = 4$

18. (2) $4e^- + BrO_3^{\ominus} \longrightarrow BrO^{\ominus}$

$x - 6 = -1 \qquad x - 2 = -1$

$x = 5 \qquad x = +1$

The reaction undergoes reduction, i.e., it acts as oxidising agent, so it requires a reducing agent.

Exercises

Single Correct Answer Type

1. (4) (1) and (2) are neutralisation reactions.

(3) The oxidation state of Cu is +2 in both reactant and product, and SO_4^{2-} ion does not change. So it is none reaction.

(4) It is a redox reaction.

$Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)

$2H^{\oplus} + 2e^- \longrightarrow H_2$ (Reduction)

2. (1) $H_2S^{2-} \longrightarrow S + 2e^-$ (Oxidation)

So H_2S is oxidised.

$4e^- + SO_2 \longrightarrow S$ (Reduction)

3. (3) It is a disproportionation reaction, so Cl_2 undergoes both oxidation and reduction.

4. (1) $\overset{+2}{O}\overset{-1\times 2}{F_2} : x - 2 = 0 \Rightarrow x = 2$

$\therefore$ Oxidation number of O = +2

5. (1) The statement is self-explanatory.

6. (3) In an aqueous medium, Li is the strongest reducing agent, since the high negative enthalpy of hydration compensates high IE_1.

7. (2) Reduction potential of $F_2 > Cl_2 > Br_2 > I_2$.

8. (3) $Ba^{2+}(H_2PO_2)_2^{-1\times 2} : H_2PO_2^{\ominus} : 2 + x - 4 = -1 \Rightarrow x = +1$

Oxidation state of P = +1

9. (4)

I. $Cs \longrightarrow Cs^{1+} + e^-$ (Oxidation)

$H_2O + e^- \longrightarrow \overset{\ominus}{O}H + \frac{1}{2}H_2$ (Reduction)

Hence, redox reaction.

II. $e^- + Cu^{2+} \longrightarrow Cu^{1+}$ (Reduction)

$2I^{\ominus} \longrightarrow I_2 + 2e^-$ (Oxidation)

Hence, redox reaction.

III. $\underset{x=-3}{\overset{\oplus}{NH_4}} \longrightarrow \underset{x=-3}{NH_3}$ (No change in oxidation number)

Hence, reaction is not redox.

IV. No change in the oxidation number of either Fe^{2+} or $CN^{\ominus}$ in both reactant and product; hence, not redox reaction.

10. (1) The balanced equation is

$2MnO_4^{\ominus} + 5C_2O_4^{2-} + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 10\,CO_2 + 8H_2O$

11. (4)

(1) $\left[Co^{+3}(N\overset{0}{H_3})_5\,Cl^{1-}\right]^{+2}Cl_2^{-1\times 2}$

$NH_3: x + 3 = 0 \Rightarrow x = -3$; oxidation state of N = −3

(2) $NH_2OH: x + 3 - 2 = 0 \Rightarrow x = -1$

Oxidation state of N = −1

(3) $(N_2H_5)_2^{+1\times 2}\,SO_4^{2-}$:

$N_2H_5^{\oplus} : 2x + 5 = +1 \Rightarrow x = -2$

Oxidation number of N = −2

(4) $\overset{+2\times 3}{Mg_3}\overset{-3\times 2}{N_2}$: Oxidation state of N = −3

12. (1) $Cr^0(CO^0)_6$ Oxidation state of Cr = 0

13. (1) Oxidation states of Ca and C are +2 and +4, respectively, in both reactant and product; hence, not redox.

(2) $4e^- + O_2 \longrightarrow 2O^{2-}$ (Reduction)

$H_2 \longrightarrow 2H^{\oplus} + 2e^-$ (Oxidation)

Hence, redox.

(3) $Na \longrightarrow Na^{\oplus} + e^-$ (Oxidation)

$2H^{\oplus} + 2e^- \longrightarrow H_2$ (Reduction)

Hence, redox.

(4) $e^- + Mn^{3+} \longrightarrow Mn^{2+}$ (Reduction)

$2Cl^{\ominus} \longrightarrow Cl_2 + 2e^-$ (Oxidation)

Hence, redox.

14. (1) The balanced equation is

$$14H^{\oplus} + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6H_2O + 3SO_2 \longrightarrow 3SO_4^{2-} + 6e^- + 12H^{\oplus}$$

$$\overline{\underline{Cr_2O_7^{2-} + 2H^{\oplus} + 3SO_2 \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O}}$$

or

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

$\therefore x = 1, y = 3, z = 1$

15. (3) $N_2H_4 \longrightarrow 2y + 10e^-$

$2x + 4 = 0 \quad 2y = 2x$

$2x = -4$

$\uparrow 2x - (-4) = 10 \uparrow$

$x = 3$

16. (2) The balanced equation is

$Cu \longrightarrow Cu^{2+} + 2e^-$ ...(i)

$H^{\oplus} + e^- + HNO_3 \longrightarrow NO_2 + H_2O$ ...(ii)

$3H^{\oplus} + 3e^- + HNO_3 \longrightarrow NO + 2H_2O$ ...(iii)

Multiplying Eq. (i) by 2 and adding Eqs. (i), (ii) and (iii), we get

$$2Cu + 4H^{\oplus} + 2HNO_3 \longrightarrow 2Cu^{2+} + NO_2 + NO + 3H_2O$$

or

$$2Cu + 6HNO_3 \longrightarrow 2Cu(NO_3)_2 + NO_2 + NO + 3H_2O$$

$\therefore x$ and y are 2 and 6.

17. (4)

(1) NO_2 $(x = 4)$, N_2O_4 $(x = 4)$

Difference in oxidation state of N = 0

(2) P_2O_5 and P_4O_{10} (Difference in oxidation state of P is zero)

(3) N_2O $(x = 1)$ and NO $(x = 2)$.

Difference in oxidation state of N = 1.

(4) SO_2 $(x = 4)$ and (SO_3) $(x = 6)$

Difference in oxidation state of S = 2

18. (4) It is a disproportionation reaction, and hence, Br_2 is both reduced and oxidised.

19. (1) $e^- + Fe^{3+} \longrightarrow Fe^{2+}$ (Reduction)

Therefore, $FeCl_3$ acts as an oxidising agent.

20. (3) $\overset{+1}{K}\left[\overset{-1}{Co}\left(\overset{0}{CO}\right)_4\right]^{1-}$

Oxidation state of Co = −1

21. (2) Reduction II is disproportionation, while I, III, and IV are not.

22. (4) II, III and IV are redox reactions.

23. (2) See solution of Q. 11 above.

Oxidation state of N in (b) is −2.

24. (3) (3) is not a disproportionation reaction.

25. (1) $\left(6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}\right)$

$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

Equivalent of $Cr_2O_7^{2-}$ = Equivalent of Sn^{2+}

$(n = 6)$ $\quad$ $(n = 2)$

$\Rightarrow$ 1 Eq = 1 Eq

$\frac{1}{6}$ mol = $\frac{1}{2}$ mol

$\frac{1}{3}$ mol of $Cr_2O_7^{2-}$ = 1 mol of Sn^{2+}

26. (3)

(1) Neutralisation

(2) It is the change of an element in one form (Oxidation state = 0) to another form.

(3) Redox reaction

(4) Physical change

27. (1) $\overset{0}{Fe}(\overset{0}{CO})_5$

Oxidation state of Fe = 0

28. (4)

Oxidation numbers of S in S^{2-}, SO_3^{2-}, SO_4^{2-}, and $S_2O_3^{2-}$ are −2, +4, +6, and +2, respectively.

(1) Difference in oxidation number of N = 0

(2) Difference in oxidation number of S = 2

(3) Difference in oxidation number of S = 6

(4) Difference in oxidation number of S = 8

29. (1) Intermolecular redox reaction and redox reactions are same. (See Q. 13 above)

30. (1) Equivalent of $MnO_4^{\ominus}$ = Equivalent of Fe (C_2O_4)

$(n = 5)$ $\quad$ $(n = 3)$

$\frac{1}{5}$ mol = $\frac{1}{3}$ mol

$\frac{3}{5}$ mol of $MnO_4^{\ominus}$ = 1 mol of Fe (C_2O_4)

0.6 mol of $MnO_4^{\ominus}$ = 1 mol of Fe (C_2O_4)

31. (1) $K \longrightarrow K^{\oplus} + e^-$ (oxidation, acts as reducing agent)

$e^- + O_2 \longrightarrow O_2^{1-}$ (reduction, acts as oxidising agent)

32. (2) It is a disproportionation reaction.

33. (3) SO_4^{2-} cannot be oxidised since the oxidation state (+6) of S is highest.

34. (4) $6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

$2I^{\ominus} \longrightarrow I_2 + 2e^-$

Oxidation state of Cr = +3

35. (2) In a basic medium,

$3e^- + MnO_4^{\ominus} \longrightarrow MnO_2$

$I^{\ominus} \longrightarrow IO_3^{\ominus} + 6e^-$

Equivalent of $MnO_4^{\ominus}$ = Equivalent of $I^{\ominus}$

$(n = 3)$ $\quad$ $(n = 6)$

1 Eq = 1 Eq

$\frac{1}{3}$ mol = $\frac{1}{6}$ mol

$\frac{6}{3}$ mol of $MnO_4^{\ominus} = 1$ mol of $I^{\ominus}$

$\therefore$ 2 mol of $MnO_4^{\ominus} = 1$ mol of $I^{\ominus}$

36. **(1)** The balanced equation is

$$\begin{array}{rcl} 12H^{\oplus} + 10e^- + 2IO_3^{\ominus} & \longrightarrow & I_2 + 6H_2O \\ 10I^{\ominus} & \longrightarrow & 5I_2 + 10e^- \\ \hline 10I^{\ominus} + 12H^{\oplus} + 2IO_3^{\ominus} & \longrightarrow & 6H_2O + 6I_2 \\ \hline \end{array}$$

$$\text{or} \quad \underset{(a)}{5I^{\ominus}} + \underset{(b)}{6H^{\oplus}} + IO_3^{\ominus} \longrightarrow \underset{(c)}{3H_2O} + \underset{(d)}{3I_2}$$

37. **(3)**

$$\begin{array}{rcl} 5e^- + MnO_4^{\ominus} & \longrightarrow & Mn^{2+} \\ M^{x+} & \longrightarrow & MO_3^{\ominus} + (5-x) \end{array}$$

$x - 6 = -1$

$x = 5$

Equivalent of $MnO_4^{\ominus}$ = Equivalent of M^{x+}

1 mol × 5 = 1.67 mol × $(5 - x)$

$\therefore x = 2$

38. **(4)** The balanced equation is

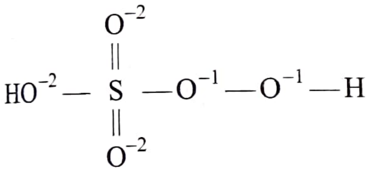
$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6K_2SO_4 + 3H_2O$$

39. **(1)** $CH_2Cl_2 : x + 2 - 2 = 0 \Rightarrow x = 0$

Oxidation state of C = 0.

40. **(2)** This is an example of iodometry.

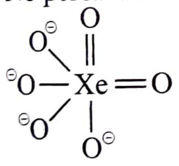
41. **(2)** H_2SO_5 is



(i.e., one peroxide bond)

Oxidation state of S = +6

42. **(1)** No peroxide bond in $[XeO_6]^{4-}$. Structure is



43. **(1)** Pr_6O_{11}:

$6x - 22 = 0$

$\therefore x = \frac{22}{6}$

44. **(2)** Xe shows +8 oxidation state in XeF_6, but it does not exist because of steric hindrance of 8 F atoms.

45. **(4)** In $CN^{\ominus}$, oxidation of C is +2, and it changes to +4 oxidation state in CO_2. So *C* is also oxidised.

46. **(4)** Disproportionation involves simultaneous oxidation and reduction of the same atom in a molecule.

47. **(4)** Intramolecular redox change involves oxidation of one atom and reduction of the other atom within a molecule.

48. **(2)** $NO_2^{\ominus} + H_2O \longrightarrow NO_3^{\ominus} + 2H^{\oplus} + 2e^-$

Balance charge on both sides.

49. **(4)** Intermolecular redox reaction involves oxidation of one molecule and reduction of the other molecule like in redox reactions.

50. **(3)** $A^{2+}B^{5+}C^{2-}$

Total positive charge = $2x + 5y$

Total negative charge = $2z$

$\therefore 2x + 5y = 2z$ ...(i)

$2x + 5y + 2z = 0$ ...(ii)

Solving Eqs. (i) and (ii), we get

$x = 3, y = 2, z = 8$

Formula is $A_3B_2C_8 = A_3(BC_4)_2$

Alternatively: Check that the total charge should be zero.

(1) $A_2(BC)_2 = 2 \times 2 + 2 \times 5 - 2 \times 2$
$= 10$ (not zero)

(2) $A_2(BC)_3 = 2 \times 2 + 3 \times 5 - 2 \times 3$
$= 13$ (not zero)

(3) $A_3(BC_4)_2 = 2 \times 3 + 2 \times 5 - 2 \times 8$
$= 0$

(4) $A_2(BC_4)_3 = 2 \times 2 + 3 \times 5 - 2 \times 12$
$= -5$ (not zero)

51. **(4)**

$$\begin{array}{rcl} 3\overset{0}{Fe} + 8e^- & \longrightarrow & (Fe^{8/3+})_3 \\ 2H^{\oplus} & \longrightarrow & \overset{0}{H_2} + 2e^-] \times 4 \\ \hline 3Fe + 4H_2O & \longrightarrow & Fe_3O_4 + 4H_2O \\ \hline \end{array}$$

Total number of electrons lost or gained is 8.

52. **(2)** $\left[Pt^{2+}(C_2\overset{0}{H_4})\overset{3-}{Cl_3}\right]^{\ominus}$

Oxidation number of Pt = +2

53. **(3)** $Mg_2P_2O_7$: $2 \times 2 + 2x - 14 = 0 \Rightarrow x = 5$

Oxidation number of P = +5

54. **(1)** Maximum oxidation number of *P* in all is +5.

55. **(3)** $2I^{\ominus} \longrightarrow I_2 + 2e^-$

$Cl_2 + 2e^- \longrightarrow 2Cl^{\ominus}$

56. **(2)** $Na_2S_4O_6$: $2 + 4x - 12 = 0$

$\therefore x = \frac{10}{4} = 2.5$

Oxidation number of S = 2.5

57. **(1)** $H_4IO_6^{\ominus} : 4 + x - 12 = -1$

$\Rightarrow x = 7$

Oxidation state of I = +7

58. **(1)** $Fe(s) \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)

$O_2 + 4H^{\oplus} + 4e^- \longrightarrow 2H_2O$ (Reduction)

Atmospheric oxidation:

$$2Fe^{2+} + 2H_2O + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 4H^{\oplus}$$

Rust is $Fe_2O_3\,x\,H_2O$

Corrosion or rusting occurs in the presence of water and air.

59. **(4)** F has the highest electronegativity.

60. **(3)** Statement is self-explanatory.

61. (4) In HNO_2, the oxidation state of N is +3. So it can go to a higher or lower oxidation state.

62. (4) $8Al \longrightarrow 8Al^{3+} + 24e^-$

$9Fe^{8/3+} + 24e^- \longrightarrow 9Fe$

63. (1) Self-explanatory.

64. (3) (1) $\left(\overset{+1}{N}H_4\right)_2 S_2O_8^{\ 2-}$

$\therefore$ Oxidation state of S = +6

(Since $S_2O_8^{2-}$ has one peroxide bond)

(2) Oxidation state of Os = +8

(3) Oxidation state of S in $H_2SO_5 = +6$

(Since it has one peroxide bond)

(4) $K^{1+}O_2^{\ 1-}$, oxidation state of O = –1/2

65. (3) CO_2 has the maximum oxidation state of +4. So it cannot go to a higher oxidation state.

66. (2) Coordination number

= Number of ligands × denticity

= 3 × 2 (bidendate)

= 6

$\overset{+3}{K_3}\left[\overset{+3}{Cr}(\overset{-2\times 3}{C_2O_4})_3\right]^{3-}$ $\therefore$ Oxidation state of Cr = +3

67. (3) $\overset{+6}{Cr}O_4^{\ 2-} \longrightarrow \overset{+6}{Cr_2}O_7^{\ 2-}$

Since oxidation state of Cr in both reactant and product is same.

68. (1) $NH_4^{\oplus} \longrightarrow N_2$

Oxidation state of N = –3 Oxidation state of N = 0

In the other reaction, the oxidation state of N decreases.

69. (1) HNC: $1 - 3 + x = 0 \Rightarrow x = 2$

Oxidation state of C = +2

70. (2) $Fe_{0.94}O$: $x \times 0.94 - 2 = 0$

$\therefore x = \frac{2}{0.94} = \frac{200}{94}$

Oxidation state of O = $\frac{200}{94}$

71. (1) $\overset{+2}{Na_2}\left[\overset{+2}{Fe}(\overset{-5}{CN})_5\overset{+1}{NO}\right]^{2-}$

Oxidation state of Fe = +2

72. (1) $Ca^{2+}(OCl^{1-})Cl^{1-}$

$OCl^{\ominus}: -2 + x = -1 \Rightarrow x = +1$

$Cl^{\ominus}: -1$

Oxidation states of Cl are –1 and +1.

73. (1)
$$\left.\begin{array}{l} Fe^{2+} \longrightarrow Fe^{3+} + e^- \\ C_2O_4^{\ 2-} \longrightarrow 2CO_2 + 2e^- \end{array}\right] n = 3$$

Equivalent weight of $FeC_2O_4 = \frac{M}{3}$

74. (4) Fe_3O_8

$3x - 16 = 0 \Rightarrow x = \frac{16}{3}$

75. (4) $\overset{0}{Fe}(\overset{0}{CO})_5$ Oxidation state of Fe = 0

76. (3) $H_2S_2O_8$: It is peroxodisulphuric acid. So oxidation state of S = +6

77. (3) (1) and (2) are disproportionation reactions.

(3) is an oxidation reaction.

$2H^{\ominus} \longrightarrow H_2 + 2e^-$

78. (1) Statement is self-explanatory.

79. (3) $e^- + MnO_4^{\ominus} \longrightarrow MnO_4^{\ 2-}$

$3e^- + MnO_4^{\ominus} \longrightarrow MnO_2$

$4e^- + 2MnO_4^{\ominus} \longrightarrow Mn_2O_3$

$5e^- + MnO_4^{\ominus} \longrightarrow Mn^{2+}$

80. (4) $Zn \longrightarrow Zn^{2+} + 2e^-$

$Ag^{\oplus} + e^- \longrightarrow Ag$

In (a), (b), and (c), oxidation number does not change.

81. (1) $S_2O_6^{\ 2-}$: $2x - 12 = -2 \Rightarrow x = 5$

$SO_3^{\ 2-}$: $x - 6 = -2 \Rightarrow x = 4$

$S_2O_4^{\ 2-}$: $2x - 8 = -2 \Rightarrow x = 3$

82. (3)
$$\begin{array}{ccc} \text{Eq of } MnO_4^{\ominus} & \equiv & \text{Eq of } H_2O_2 \\ (n = 5) & & (n = 2) \\ \frac{1}{5}\text{ mol} & = & \frac{1}{2}\text{ mol} \end{array}$$

1 mol of $MnO_4^{\ominus} = \frac{5}{2}$ mol of H_2O_2

83. (2) $M^{3+} \longrightarrow M^{6+} + 3e^-$

84. (1) Oxidation state of C in $CO_3^{\ 2-}$ is +4, which is maximum. So, it will not be oxidised.

85. (3)
$$\begin{array}{ccc} \text{Eq of } Cr_2O_7^{\ 2-} & \equiv & \text{Eq of } Sn^{2+} \\ (n = 6) & & (n = 2) \\ \frac{1}{6}\text{ mol} & = & \frac{1}{2}\text{ mol} \end{array}$$

$\frac{1}{3}$ mol of $Cr_2O_7^{\ 2-}$ = 1 mol of Sn^{2+}

86. (3) Oxidation state of C in CO_2 is +4, which is maximum. So it does not undergo oxidation, and hence, it is not a reducing agent.

87. (3) $\left[\overset{0}{Cr}(\overset{0}{PPh_3})_3(\overset{0}{CO})_3\right]$

Oxidation state of Cr = 0

88. (3) Balance the equation

$3Cl_2 + 6\overset{\ominus}{OH} \longrightarrow ClO_3^{\ominus} + 5Cl^{\ominus} + 3H_2O$

89. (2) PbO_2 is a powerful oxidising agent and liberates O_2 when treated with acids.

$PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$

$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$

90. (3) SO_2 is an oxidising agent.

$4e^- + SO_2 \longrightarrow S$

Equivalent of $SO_2 = \frac{64}{4} = 16$.

91. (3) $5e^- + ClO_2 \longrightarrow Cl^{\ominus}$

Eq of ClO_2 = Eq of H_2O_2

$(n = 5)$ $(n = 2)$

$\frac{1}{5}$ mol $\equiv \frac{1}{2}$ mol

1 mol of ClO_2 = $\frac{5}{2}$ mol of H_2O_2

Multiple Correct Answers Type

1. **(3, 4)**

(1) $\overset{+6}{CrO_3}$ (Maximum oxidation state, cannot be oxidised further)

(2) $\overset{+3}{Al_2O_3}$ (Maximum oxidation state, cannot be oxidised further)

(3) $\overset{+4}{SO_2} \longrightarrow \overset{+6\ 2-}{SO_4}$ (Can be oxidised further)

(4) $\overset{+6}{MnO_3} \longrightarrow \overset{+7}{MnO_4}^{\ominus}$ (Can be oxidised further)

2. **(1, 3)**

Statements are self-explanatory.

3. **(1, 2, 3, 4)**

All statements are self-explanatory.

4. **(1, 2)**

In (1), $MnO_4^{\ominus} \longrightarrow MnO_2$ occurs only in basic medium

In (2), $Cr(OH)_2 \longrightarrow Cr(OH)_3$ occurs only in basic medium.

(3) and (4) occur only in acidic medium.

5. **(1, 2, 3)** (1) Oxidation state of K is +1 in both reactant and product.

In (2), oxidation state of Cr (+6) does not change.

In (3), oxidation states of Ca and C and O do not change.

In (4), the H_2O_2 which disproportionates is both oxidising and a reducing agent.

6. **(1, 3, 4)**

Reduction potential of $F_2 > Cl_2 > Br_2 > I_2$.

So F_2 can displace $Cl^{\ominus}$, $Br^{\ominus}$, and $I^{\ominus}$ but not vice versa.

Similarly, Cl_2 can displace $Br^{\ominus}$ and $I^{\ominus}$ but not vice versa and Br_2 can displace only $I^{\ominus}$ but not vice versa.

In (a), Fe (not Fe^{2+}) is a better reducing agent than $I^{\ominus}$.

7. **(1, 4)**

(1) Since I_2 is reduced to $I^{\ominus}$, so H_2O_2 must be oxidised to O_2. (Oxidation state of O is zero)

$$H_2O_2 + I_2 \longrightarrow 2I^{\ominus} + O_2 + 2H^{\oplus}$$

(4) Sn^{2+} is oxidised to Sn^{4+}, so H_2O_2 must be reduced to H_2O. (Oxidation state of O is –2)

$$2H^{\oplus} + H_2O_2 + Sn^{2+} \longrightarrow Sn^{4+} + 2H_2O$$

8. **(1, 3)**

(1) The MnO_4^{2-} is reduced to Mn^{2+}, so it must also be oxidised to Mn^{7+} ($MnO_4^{\ominus}$) since $H^{\oplus}$ is already in its maximum oxidation state.

$$5MnO_4^{2-} + 8H^{\oplus} \longrightarrow Mn^{2+} + 4MnO_4^{\ominus} + 4H_2O$$

(3) NO_2 disproportionates to NO and $NO_3^{\ominus}$. (Oxidation state of N is +5)

$$3NO_2 + H_2O \longrightarrow NO + 2NO_3^{\ominus} + 2H^{\oplus}$$

9. **(1, 3, 4)** $4H_2O + \overset{+1\times 3}{Cu_3}\,\overset{-3}{P} \longrightarrow 3Cu^{2+} + H_3PO_4 + 11e^- + 5H^{\oplus}] \times 6$

$$6e^- + 14\,H^{\oplus} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O] \times 11$$

$$6\,Cu_3P + 124H^{\oplus} + 11\,Cr_2O_7^{2-} \longrightarrow 18Cu^{2+} + 6H_3PO_4 + 22\,Cr^{3+} + 53H_2O.$$

10. **(1, 2, 3, 4)** All statements are self-explanatory.

11. **(1, 3, 4)** Refer solved example 2.2(c).

12. **(1, 2, 3, 4)**

(1) PbO_2 is a powerful oxidising agent and liberates O_2 with acids.

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$$

(2) $PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$

(3) $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$

(4) $Pb_3O_4 + 4HNO_3 \longrightarrow Pb(NO_3)_2 + PbO_2 + 2H_2O$

13. **(2, 3, 4)**

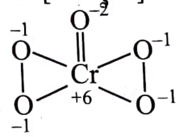
(1) In Cu_2O and Cu_2S, the oxidation state of Cu is +1. So they are reduced to Cu^0. ($Cu^{1+} + e^- \longrightarrow Cu^0$)

14. **(2, 3)**

(1) $Fe^{+2}\,(Cr_2O_4)^{2-}$: Oxidation state of Cr = +3

(2) $K^{\oplus}\,[CrO_3Cl]^{\ominus}$: Oxidation state of Cr = +6

(3)



Oxidation state of Cr = +6. (Two peroxo linkage)

(4) $[Cr(OH)_4]^{\ominus}$: Oxidation state of Cr = +3

15. **(1, 2, 3, 4)**

(1) CH_2O: $x + 2 - 2 = 0 \Rightarrow x = 0$; Oxidation state of C = 0.

(2) CH_2Cl_2: $x + 2 - 2 = 0 \Rightarrow x = 0$.

Oxidation state of C = 0

(3) $C_6H_{12}O_6$: $6x + 12 - 12 = 0 \Rightarrow x = 0$

Oxidation state of C = 0

(4) $C_{12}H_{22}O_{11}$: $12x + 22 - 22 = 0 \Rightarrow x = 0$

Oxidation state of C = 0

16. **(1, 3)**

(1) Oxidation state of S:

$H_2S_2O_7$: $2 + 2x - 14 = 0 \Rightarrow x = 6$

$Na_2S_4O_6$: $2 + 4x - 12 = 0 \Rightarrow x = 2.5$

$Na_2S_2O_3$: $2 + 2x - 6 = 0 \Rightarrow x = 2$

S_8: $8x = 0 \Rightarrow x = 0$

(3) H_2SO_5 (Peroxo linkage)

Oxidation state of S = +6

H_2SO_3: $2 + x - 6 = 0$

Oxidation state of S = +4

SCl_2: $x - 2 = 0$

Oxidation state of S = +2

H_2S: $2 + x = 0$

Oxidation state of S = –2

17. **(4)** COOH: $x - 4 + 1 = 0 \Rightarrow x = 3$

Oxidation state of C in COOH = +3

18. (1, 2, 3) (1), (2), and (3) are autoredox or disproportionation reaction.

19. (1, 2, 3, 4) Statement are self-explanatory.

20. (1, 2, 3, 4)

$$4KO_2 + 2H_2O \longrightarrow 4KOH + 3O_2$$

[Hydrolysis, disproportionation and redox]

$4KOH + 4CO_2 \longrightarrow 4KHCO_3$ (Acid–base reaction)

21. (1, 2, 3, 4) The element in a molecule having its oxidation state in the middle (i.e., greater than minimum and less than maximum) can be used as an oxidising agent and a reducing agent both.

22. (1, 2, 4) The highest oxidation state is given by the group number except F and O.

23. (2, 3) The lowest oxidation state is given by the group number –8 except metals.

24. (1, 2, 4)

The average oxidation state is taken if both oxidation state are positive or negative including zero.

25. (1, 3) In tailing of Hg, it loses its meniscus and sticks to glass, due to solubility of Hg_2O in Hg, when Hg gets oxidised to Hg_2^{2+} by O_3. It is removed by H_2O_2.

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$

$$Hg_2O + H_2O_2 \longrightarrow 2Hg + H_2O + O_2.$$

26. (3, 4)

(3) $2e^- + ClO^{\ominus} \longrightarrow Cl^{\ominus}$ (Reduction)

$x - 2 = -1 \qquad x = -1$

$x = +1$

$ClO^{\ominus} \longrightarrow ClO_3^{\ominus} + 4e^-$ (Oxidation)

$x = 1 \qquad x = 5$

(4) In $HCuCl_2$, Cu is in +1 oxidation state which disproportionates to Cu^{2+} and Cu^0.

27. (2, 3, 4)

(2) $S^{2-} \longrightarrow S + 2e^-$ (Oxidised)

$3e^- + NO_3^{\ominus} \longrightarrow NO$ (N is reduced and HNO_3 is oxidising agent)

28. (2, 3, 4)

(2) $3H_2O + \overset{0}{P_4} + 3\overset{\ominus}{O}H \longrightarrow \overset{-3}{P}H_3 + 3H_2\overset{+1}{P}O_2^{\ominus}$

(3) $S_8^0 + 12\overset{\ominus}{O}H \longrightarrow 4S^{2-} + 2\overset{+2}{S}_2O_3^{2-} + 6H_2O$

(4) $\overset{0}{Br_2} + 2\overset{\ominus}{O}H \longrightarrow \overset{+1}{Br}O^{\ominus} + \overset{-1}{Br}^{\ominus} + H_2O$

29. (2, 3, 4)

(2), (3), and (4) are redox reactions.

In (1), there in no change in the oxidisation state (+6) of Cr.

30. (2, 3)

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$ (Oxidation)

$I_2 + 2e^- \longrightarrow 2I^{\ominus}$ (Reduction)

31. (1, 2, 4) Same explanation as in answer of Q. 21 above.

32. (3, 4) In both (3) and (4), the oxidation numbers of the various elements in the molecule do not change.

Linked Comprehension Type

1. (4) Oxidation state of X = – 2 ⇒ $\overset{+2}{A}\overset{-2}{X}$

Oxidation state of O = –2 ⇒ $\overset{-2}{O}\overset{+2}{Y}$

Oxidation state of X = – 2, ⇒ $\overset{-2\times2}{X_2}\overset{+4}{B}$

$$\overset{+2}{A}\overset{-2}{X} + BY + H_2O \longrightarrow \overset{+1}{H}\overset{-1}{A} + \overset{-2}{O}\overset{+2}{Y} + \overset{-2\times2}{X_2}\overset{+4}{B}$$

∴

$$e^- + A^{2+} \longrightarrow A^{1-} \text{ (reduction)}$$

$$\overset{+a}{B}\,\overset{-a}{Y} \longrightarrow B^{4+} + Y^{2+} \text{ (oxidation)}$$

Therefore, B or Y or both might have been oxidised.

2. (4) In BY, the oxidation state of B ≤ +4

Oxidation state of Y ≤ +2.

If the oxidation state of B is +1 and that of Y is –1, then both will be oxidised.

If the oxidation state of B is +2 and that of Y is –2, then both will be oxidised.

If the oxidation state of B is +3 and that of Y is –3, then both will be oxidised.

3. (2) $A^{2+} + \cancel{H^{\oplus}} + \cancel{3e^-} \longrightarrow HA] \times 2$

$BY + H_2O \longrightarrow B^{4+} + OY + \cancel{2H^{\oplus}} + \cancel{6e^-}$

$2A^{2+} + BY + H_2O \longrightarrow 2HA + B^{4+} + OY$

or

$$\underset{2}{\underline{2AX}} + \underset{1}{\underline{BY}} + \underset{1}{\underline{H_2O}} \longrightarrow \underset{2}{\underline{2HA}} + \underset{1}{\underline{BX_2}} + \underset{1}{\underline{OY}}$$

$2 + 1 + 1 + 2 + 1 + 1 = 8$

The sum of all the coefficients is 8.

4. (4)

(1) $Cr_2O_7^{2-}$ (orange red) oxidises SO_2 to SO_4^{2-} and is itself reduced to Cr^{+3} (green).

$$Cr_2O_7^{2-} + 3H^{\oplus} + 3SO_2 \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

(Orange) (Green)

(2) Both reacts together

$$\overset{+2}{Hg}Cl_2 + \overset{+2}{Sn}Cl_2 \longrightarrow \overset{+1}{Hg_2}Cl_2\downarrow + \overset{+4}{Sn}Cl_4$$

(White ppt)

$$\overset{+1}{Hg_2}Cl_2 + \overset{+2}{Sn}Cl_2 \longrightarrow 2Hg\downarrow + \overset{+4}{Sn}Cl_4$$

(Grey)

(3) $\overset{0}{Fe} + \overset{+2}{Cu}\overset{2}{S}O_4 \longrightarrow Fe^{2+} + \overset{0}{Cu}$

(Blue)

(4) $[CuCl_4]^{2-}$ is formed but $[CuI_4]^{2-}$ is not.

$I^{\ominus}$ ion reduces Cu^{2+} to $\overset{+1}{Cu}I$ and itself undergoes oxidation to form I_2. However, $Cl^{\ominus}$ does not reduce Cu^{2+}.

5. (4)

(1) The purple colour of $KMnO_4$ is decolourised due to the reduction of $MnO_4^{\ominus}$ to Mn^{2+} and $C_2O_4^{2-}$ is oxidised to CO_2 in acidic medium.

$$2MnO_4^{\ominus} + 16H^{\oplus} + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Reduction (oxidising agent)

(2) $Br_2 + 2I^{\ominus} \longrightarrow 2Br^{\ominus} + I_2$

Oxidation (Reducing agent)

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$$

(3) $4x - 12 = -4$ $\quad$ $4x - 12 = -2$

$4x = 8$ $\quad$ $4x = 10$

$10 - 8 = 2$

Change in oxidation number of each N $= \dfrac{2}{4} = 0.5$

(4) $\underline{C}H_4 : x + 4 = 0, x = -4$

$\underline{C}O_2 : x - 4 = 0, x = 4$

6. (1)

(1) An element in the lowest oxidation state can only attain higher oxidation state. So it is a reductant and undergoes oxidation.

(2) An element in the highest oxidation state can only attain lower oxidation state. So it is an oxidant and undergoes reduction.

(3) The oxidation state of Rb and K is +1 (first group element)

$$\overset{+1\times4}{Rb_4}\,\overset{+1}{K}\,[HV_{10}O_{28}]^{-5}$$

$HV_{10}O_{28}^{-5} = 1 + 10x - 2 \times 28 = -5$

$\therefore$ Oxidation state of $V(x) = 5$

(4) Calomel is $\overset{+1\times2}{Hg_2}\ \overset{-1\times2}{Cl_2}$

The oxidation number of Hg is +1 and valency is 2.

7. (1) (1) **Wrong:** The algebraic sum of the oxidation numbers of all the atoms in an ion equals the charge present on the ion.

(2) True statement

(3) True ($2Cl^{\ominus} \longrightarrow Cl_2 + 2e^-$) (oxidation)

(4) True

8. (3)

(1) **Disproportionation reaction:**

$$\overset{0}{Br_2} \longrightarrow \overset{-1}{2Br^{\ominus}}$$

(Oxidation state of Br_2 decreases from 0 to –1.)

$$\overset{0}{Br_2} \longrightarrow BrO_3^{\ominus}$$

$x - 6 = -1$

$x = 5$

(Oxidation state of Br_2 increases from 0 to +5.)

(2) **Disproportionation reaction:**

$\overset{+1}{Cu_2O} \longrightarrow \overset{0}{Cu}$ (Oxidation state of Cu decreases from +1 to 0)

$ \longrightarrow Cu^{2+}$ (Oxidation state of Cu increases from +1 to +2)

(3) **Oxidation:**

$$\overset{+2}{CN^{\ominus}} \longrightarrow \overset{+4}{CO_3^{2-}} + 2e^-$$

$x - 3 = -1$ $\quad$ $x - 6 = -2$

$x = 2$ $\quad$ $x = 4$

$$CN^{\ominus} \longrightarrow NO_3^{\ominus} + 8e^-$$

(Oxidation state of N = – 3) $x - 6 = -1$

$x = 5$

Both are oxidation.

(4) **Disproportionation reaction:**

$(CN)_2$ gets simultaneously oxidised to $CNO^{\ominus}$ (cyanate ion) and reduced to $CN^{\ominus}$.

The oxidation number of N in $(CN)_2$ is –3, in $CN^{\ominus}$ is –2, and in $CNO^{\ominus}$ is –5.

9. **(1)** Carbon in diamond is in elemental state, so the oxidation state of C in diamond is zero.

10. **(4)**

(1) $H_2C{=}C{=}O$ (Ketenes) (Valency of C = 4)

(2) $R_2C{=}CR_2$ (Alkenes) (Valency of C = 4)

(3) $H_2C{=}C{=}CH_2$ (Allenes) (Valency of C = 4)

(4) $:CH_2$ (Carbenes) (Valency of C = 2)

11. **(4)**

(1) $\overset{-4\ +1\times4}{CH_4}$ oxidation state of C = – 4

(2) $CH_3OH : x + 4 - 2 = 0 \Rightarrow x = -2$

(3) $HCOOH : x + 2 - 4 = 0 \Rightarrow x = 2$

(4) $C_6H_{12}O_6$: $6x + 12 - 12 = 0 \Rightarrow x = 0$

12. **(1)**

(1) $\overset{+2}{H\,C}OOH$

(2) $\overset{0}{C}H_2O : x + 2 - 2 = 0 \Rightarrow x = 0$

(3) $\overset{-2}{C}H_3OH : x + 4 - 2 = 0 \Rightarrow x = -2$

(4) $\overset{-4\ +1\times4}{CH_4}$: oxidation state of C = –4

13. **(3)** Highest oxidation state of C is in (a)

C_3O_2 (Carbon suboxide): $3x - 4 = 0 \Rightarrow x = \dfrac{4}{3}$

14. **(a → q)** $\overset{-4}{C}H_4 \longrightarrow \overset{-2}{C}H_3OH$

(Increase in oxidation number from –4 to –2) (Oxidation)

(b → p) $\overset{0}{C}H_2Cl_2 \longrightarrow \overset{0}{C}H_2O$

(Oxidation number is zero for both) (Neither)

(c → r) $\overset{-2}{C}H_2{=}\overset{-2}{C}H_2 \longrightarrow H_3\overset{-3}{C}{-}\overset{-3}{C}H_3$

(Decrease in oxidation number from –2 to –3 for both C) (Reduction)

(d → p) $H\overset{-1}{C}{\equiv}\overset{-1}{C}H \longrightarrow H_3\overset{-3}{C}{-}\overset{+1}{C}HO$

The oxidation number of both C's has changed one from –1 to –3 and in the other from –1 to +1. Thus the average value is compared for both reactant and product, which is –1. It has remained unchanged, so it is neither.

$$C_2H_2 \longrightarrow CH_3CHO$$
$$2x + 2 = 0 \qquad 2x + 4 - 2 = 0$$
$$x = -1 \qquad x = -1$$

15. (4) $\overset{+1\times4}{K_4}\left[Fe^{2+}\overset{-1\times6}{(CN)_6}\right]^{-4}$ Oxidation state of Fe is +2.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$6(CN)^{\ominus} \longrightarrow 6CO_2 + 12e^-$$
$$6(x - 3 = -1) \quad 6(x - 4 = 0)$$
$$6(x = 2) \qquad 6(x = 4)$$
$$6(CN)^{\ominus} \longrightarrow 6NO_3^{\ominus} + 48e^-$$
$$\begin{pmatrix}\text{Oxidation number}\\ \text{of N} = -3\end{pmatrix} \quad 6(x - 6 = -1)$$
$$6(x = 5)$$

$$[Fe^{+2}(CN)_6]^{4-} \longrightarrow Fe^{+3} + 6CO_2 + 6NO_3^{\ominus} + 61e^-$$

16. (2)

$$\left.\begin{array}{lll} Fe^{2+} \longrightarrow & Fe^{3+} + e^- & \\ S_2^{2-} \longrightarrow & 2SO_2 & +10e^- \\ 2x = -2 & 2x - 8 = 0 & \\ & 2x = 8 & \end{array}\right] \text{Total } e^- = 11$$

17. (4)

$$\left.\begin{array}{lll} Br_2 \longrightarrow & 2BrO_3^{\ominus} & +10e^- \\ 2x = 0 & 2x - 12 = -2 & \\ & 2x = 10 & \\ 2e^- + Br_2 \longrightarrow & 2Br^{\ominus}] \times 5 & \end{array}\right]$$

$$6Br_2 \longrightarrow 2BrO_3^{\ominus} + 10Br^{\ominus}$$

$$\text{Equivalent weight of } Br_2 = \frac{6\,[Br_2]}{10} = \frac{3}{5}$$

$$n\text{-factor} = \frac{5}{3}$$

18. (2)

$$As_2^{3+} \longrightarrow 2\,As^{5+} + 4e^-$$
$$2x = 6 \qquad 2x = 10$$
$$S_3^{2-} \longrightarrow 3SO_4^{2-} + 24e^- \quad n\text{-factor} = 28$$
$$3x = -6 \qquad 3x - 24 = -6$$
$$3x = 18$$

19. (1, 3)

(1)
$$3e^- + Mn^{7+} \longrightarrow Mn^{4+} \quad \text{(Reduction)}$$
$$2O^{2-} \longrightarrow O_2 + 4e^- \text{(Oxidation)}$$

Hence, it is an intramolecular redox reaction.

(2) It is an oxidation reaction in which Fe^{2+} is oxidised to Fe^{3+} and $CN^{\ominus}$ is oxidised to CO_2 and $NO_3^{\ominus}$.

(3) It is an intramolecular redox reaction.

$$2e^- + Hg^{2+} \longrightarrow Hg \quad \text{(Reduction)}$$
$$2O^{2-} \longrightarrow O_2 + 4e^- \text{(Oxidation)}$$

(4) It is a disproportionation reaction.

20. (1, 2, 3)

(1)
$$2e^- + Cl_2 \longrightarrow 2Cl^{\ominus} \text{ (Reduction)}$$
$$2ClO^{\ominus} + 2e^- \text{ (Oxidation)}$$
[Disproportionation]

(2) It is also a disproportionation reaction.

$$\left[\overset{+1}{H}\,\overset{+1}{Cu}\,\overset{-1\times2}{Cl_2}\right]$$
$$e^- + Cu^{1+} \longrightarrow Cu \quad \text{(Reduction)}$$
$$Cu^{1+} \longrightarrow Cu^{2+} + e^- \text{(Oxidation)}$$

(3) It is also a disproportionation reaction.

HCHO is oxidised to $HCOO^{\ominus}$ and reduced to CH_3OH.

(4) It is none since the oxidation state of Mg is +2 in both reactant and product. Similarly, the oxidation states of C and O are +4 and –2 in both reactant and product.

21. (1, 2, 3)

(1) It is an intermolecular redox reaction.

$$2I^{\ominus} \longrightarrow I_2 + 2e^- \text{ (Oxidation)}$$
$$10e^- + 2IO_3^{\ominus} \longrightarrow I_2 \quad \text{(Reduction)}$$

(2) It is also an intermolecular redox reaction.

$$Fe \longrightarrow Fe^{2+} + 2e^- \text{(Oxidation)}$$
$$2e^- + N_2H_4 \longrightarrow 2NH_3 \quad \text{(Reduction)}$$
$$2x = -4 \qquad 2x = -6$$

(3) It is also an intermolecular redox reaction.

$$8e^- + NO_3^{\ominus} \longrightarrow \overset{\oplus}{NH_4} \text{ (Reduction)}$$
$$x = 5 \qquad x + 4 = +1$$
$$x = -3$$
$$S^{2-} \longrightarrow HSO_4^{\ominus} + 8e^- \text{(Oxidation)}$$
$$x = -2 \qquad 1 + x - 8 = -1$$
$$x = 6$$

(4) It is none, since the oxidation state of Cr in both reactant and product is +6.

22. (1, 2, 3, 4)

(1), (2), and (3) are auto or induced redox reaction.

(4) is a disproportionation reaction.

23. (1, 2, 3, 4)

All are none reactions since in all the reactions the oxidation states of reactant and product do not change.

24. (1, 2, 3, 4)

All statements are correct.

$Cl^{\ominus}$ ion remains unchanged. It is a spectator ion.

25. (1, 2, 3, 4)

Spectator ions in (1), (2), and (3) are SO_4^{2-} ions while in (4), it is $Cl^{\ominus}$ ion, since all of them remain unchanged.

Matrix Match Type

1. (a → q)
$$Mn^{2+} \longrightarrow Mn^{4+} + 2e^- \text{ (Oxidation)}$$
$$2e^- + H_2O_2 \longrightarrow 2H_2O \text{ (Reduction)}$$

(b → r)
$$\overset{0}{3K} \longrightarrow 3K^{\oplus} + 3e^- \text{ (Oxidation)}$$
$$3e^- + Al^{3+} \longrightarrow Al \text{ (Reduction)}$$

(c → p)
$$\overset{0}{3Fe} \longrightarrow Fe_3O_4 + 8e^- \text{ (Oxidation)}$$
$$3x = 0 \qquad 3x - 8 = 0$$
$$3x = 8$$
$$8e^- + 4H_2O \longrightarrow 4H_2 \text{ (Reduction)}$$
$$8x - 8 = 0 \qquad 8x = 0$$
$$8x = 8$$

(d → s)
$$3H_2S \longrightarrow 3S + 6e^-$$
$$2 + x = 0 \qquad x = 0$$
$$x = -2$$

$$6e^- + 2NO_3^{\ominus} \longrightarrow 2NO$$
$$x - 6 = -1 \qquad x - 2 = 0$$
$$x = 5 \qquad x = 2$$

2. **(a → r)** $Fe_4^{3+}[Fe^{2+}(CN)_6]_3$

Average oxidation number of Fe is

$$\frac{3 \times 4 + 2 \times 3}{7} = \frac{18}{7}$$

(b → q) $Fe_2^{2+}[Fe^{2+}(CN)_6]$

Average oxidation number of Fe is

$$\frac{2 \times 2 + 2}{3} = \frac{6}{3} = 2$$

(c → p) $Fe_3^{2+}[Fe^{3+}(CN)_6]_2$

Average oxidation number of Fe is

$$\frac{2 \times 3 + 3 \times 2}{5} = \frac{12}{5}$$

(d → t) $Fe^{3+}[Fe^{3+}(CN)_6]$

Average oxidation number of Fe is

$$\frac{3 + 3}{2} = \frac{6}{2} = 3$$

(e → q) $Na_2^{2+}[Fe^{2+}(CN^{5-})_5\,NO^{1+}]^{2-}$

Oxidation state of Fe is +2.

Note: Here NO is in +1 oxidation state.

(f → s) $[Fe^{1+}(NO^{1+})(\overset{0}{H_2O})_5]^{2+}\,SO_4^{2-}$

Oxidation state of Fe is +1.

(g → u) Fe_3O_4 :

$$3x - 8 = 0$$
$$\Rightarrow x = \frac{8}{3}$$

Therefore, oxidation state of Fe is 8/3.

3. **(a → r)**

$$2e^- + I_2 \longrightarrow 2I^{\ominus} \text{ (Reduction and acts as an oxidant)}$$
$$I_2 \longrightarrow 2IO_3^{\ominus} + 10e^- \text{ (oxidation and acts as a reductant)}$$
$$2x = 0 \qquad 2x - 12 = -2$$
$$2x = 10$$

So I_2 acts both as an oxidant and a reductant.

(b → p) No change in the oxidation number of either of the conjugate pairs.

$$Ba^{2+}Cl_2^{2-} \longrightarrow Ba^{2+}SO_4^{2-}$$
$$Na_2^{2+}SO_4 \longrightarrow 2\overset{+2}{Na}Cl$$

(None is an oxidant or a reductant)

(c → s) In a conjugate pair, the oxidant has a higher oxidation number.

For $AlCl_3$: $Al^{3+} + 3e^- \longrightarrow Al^0$

(Reduction and acts as an oxidant)

For Na: $Na \longrightarrow Na^{\oplus} + e^-$

(Oxidation and acts as a reductant)

(d → q) For SO_2 : $4e^- + SO_2 \longrightarrow S^0$

(Reduction and acts as an oxidant)

For H_2S: $S^{2-} \longrightarrow S^0 + 2e^-$

(Oxidation and acts as a reductant)

4. **(a → q)** Refer solved example 2.6 (a)

(b → s) Refer solved example 2.6 (e)

(c → p) Refer solved example 2.6 (f)

(d → u) Refer solved example 2.6 (i)

(e → r) Refer solved example 2.6 (p)

(f → t) Refer solved example 2.6 (q)

5. **(a → r)** Refer solved example 2.6 (b)

(b → s) Refer solved example 2.6 (d)

(c → p) Refer solved example 2.6 (g)

(d → t) Refer solved example 2.6 (h)

(e → q) Refer solved example 2.6 (n)

6. **(a → q)** Conc HNO_3 with metals gives NO_2.

$$e^- + NO_3^{\ominus} \longrightarrow NO_2\ (n = 1)$$

(b → p) Dil HNO_3 with metals except Zn gives NO.

$$3e^- + NO_3^{\ominus} \longrightarrow NO\ (n = 3)$$

(c → s) Dil HNO_3 with Zn, Fe, and Sn gives N_2O.

$$8e^- + 2NO_3^{\ominus} \longrightarrow N_2O\ (n = 8)$$

(d → r) Zn, Fe, and Sn with very dil HNO_3 give $NH_4^{\oplus}$ and with cold dil HNO_3 give NH_2OH.

$$8e^- + NO_3^{\ominus} \longrightarrow NH_4^{\oplus}\ (n = 8)$$
$$6e^- + NO_3^{\ominus} \longrightarrow NH_2OH\ (n = 6)$$

(e → u) Moderately conc HNO_3 with Fe gives ferric nitrate and NO_2.

(f → t) Fe, Al, Co, Ni, and Cr with conc HNO_3 are passive.

(g → w) Sn with conc HNO_3 gives metastannic acid (H_2SnO_3) and NO_2.

(h → v) Mg, Sn, and Ca with dil. HNO_3 give metal nitrates and H_2.

(i → x) Au and Pt with aqua regia give $AuCl_4^{\ominus}$, $PtCl_6^{2-}$, and NO.

7. **(a → q)** $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

(b → r) $S_2O_3^{2-} + 10\overset{\ominus}{O}H \longrightarrow 2SO_4^{2-} + 5H_2O + 8e^-$

(c → p) $5H_2O + S_2O_3^{2-} \longrightarrow 2HSO_4^{\ominus} + 8H^{\oplus} + 8e^-$

(d → t) $5e^- + 8H^{\oplus} + MnO_4^{\ominus} \longrightarrow Mn^{2+} + 4H_2O$

(e → u) $e^- + MnO_4^{\ominus} \longrightarrow MnO_4^{2-}$

(f → s) $3e^- + 4H^{\oplus} + MnO_4^{\ominus} \longrightarrow MnO_2 + 2H_2O$

8. **(a → p)** $2Cu \longrightarrow 2Cu^{2+} + 4e^-]$ Oxidation

$$2Cu + 4HNO_3 \longrightarrow 2Cu(NO_3)_2 + 4e^- + 4H^{\oplus} \quad \text{...(i)}$$

$$\left.\begin{array}{l} e^- + HNO_3 \longrightarrow NO_2 \\ 3e^- + HNO_3 \longrightarrow NO \end{array}\right] \text{Reduction}$$

$$\overline{\underline{4e^- + 2HNO_3 \longrightarrow NO_2 + NO}} \quad \text{...(ii)}$$

Adding Eqs. (i) and (ii), we get

$$2Cu + 6HNO_3 \longrightarrow 2Cu\,(NO_3)_2 + NO + NO_2 + 4H^{\oplus}$$

x and y are 2 and 6.

(b → q) Refer solved example 2.2(a).

$$2I^{\ominus} \longrightarrow I_2 + 2\cancel{e}\;] \times 3 \text{ (Oxidation)}$$

$$3\cancel{e} + CrO_4^{2-} \longrightarrow Cr^{+3}] \times 2 \text{ (Reduction)}$$

$$6I^{\ominus} + 2CrO_4^{2-} \longrightarrow 3I_2 + 2Cr^{3+}$$

x and y are 6 and 2.

(c → r) Refer solved example 2.2 (d).

x and y are 3 and 28.

(d → s) $3e^- + P \longrightarrow PH_3$ (Reduction)

$$3P \longrightarrow 3H_2PO_2^{\oplus} + 3e^- \text{ (Oxidation)}$$

$$4P \longrightarrow PH_3 + 3H_2PO_2^{\oplus}$$

x and y are 1 and 3

(e → t)

$$8I^{\ominus} \longrightarrow 4I_2 + 8\cancel{e}\;] \text{ (Oxidation)}$$

$$8H^{\oplus} + 8\cancel{e} + SO_4^{2-} \longrightarrow S^{2-} + 4H_2O] \text{ (Reduction)}$$

$$8H^{\oplus} + 8I^{\ominus} + SO_4^{2-} \longrightarrow 4I_2 + S^{2-} + 4H_2O$$

or

Adding $2H^{\oplus}$ and $8K^{\oplus}$ to both sides, we get

$$8KI + H_2SO_4 + 8H^{\oplus} \longrightarrow 4I_2 + H_2S + 4H_2O + 8K^{\oplus}$$

Now adding $4\,SO_4^{2-}$ to both sides, we get

$$8KI + H_2SO_4 + 4H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O + 4K_2SO_4$$

or

$$8KI + 5H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O + 4K_2SO_4$$

x and y are 8 and 5.

9. **(a → t, u) Disproportionation or auto-redox:** One molecule of a reactant is oxidised and reduced simultaneously.

(b → p) C_3O_2 (Fractional oxidation number):

$$3x - 4 = 0 \Rightarrow x = \frac{4}{3}$$

(c → s) CH_2Cl_2 (Zero oxidation number):

$$x + 2 - 2 = 0;\ x = 0$$

(d → q) Redox reaction:

$(Mn^{4+} + 2e^- \longrightarrow Mn^{2+})$ (Reduction)

$(2Cl^{\ominus} \longrightarrow Cl_2 + 2e^-)$ (Oxidation)

(e → r) Photosynthesis is also a redox reaction occurring in nature.

10. **(a → r, t)** Both processes are redox reaction or intermolecular redox.

(b → r, t) Again, both processes are redox or intermolecular redox reactions.

(c → p) Both processes involve physical changes. The production of O_3 from O_2 by lightning is the change of an element in one form (oxidation state = 0) to another form (oxidation state = 0) and is also called allotropy.

(d → q) It is an acid–base reaction or neutralisation reaction.

(e → s) **Intramolecular redox reaction:** One atom of a molecule is oxidised and the other atom is reduced.

(f → r, t) **Intermolecular redox reaction:** It is both redox and intermolecular redox reaction.

Numerical Value Type

1. **(3)** The +3 oxidation state of the underlined element is in (b), (g), and (h).

a. +5 **b.** +3 **c.** +5 **d.** +1 **e.** +8

f. +2 **g.** +3 **h.** +3

2. **(2)** The +5 oxidation state of the underlined element is in (a) and (c).

3. **(3)** The zero oxidation state of the underlined element is in (b), (c), and (e).

a. +4 **b.** 0 **c.** 0 **d.** +6 **e.** 0

4. **(10)** See answer of Q. 3. The sum of the oxidation states of all the underlined elements is 4 + 0 + 0 + 6 + 0 = 10.

5. **(4)** The maximum oxidation state is the group number. The minimum oxidation state for metals is zero; for non-metals it is equal to the group number minus 8. The maximum and the minimum oxidation states are

a. +5, 0 **b.** +6, –2 **c.** +7, 0 **d.** +4, 0 **e.** +3, 0

6. **(6)** Species which are very good oxidising agents are

a. F_2 **e.** $MnO_4^{\ominus}$ **h.** Ce^{4+} **i.** $Cr_2O_7^{2-}$ **j.** CrO_4^{2-}

f. HNO_3

7. **(3)** Species which are very good reducing agents are

c. Na **f.** $I^{\ominus}$ **l.** Fe^{2+}

8. **(3)** Species which are neither oxidising agent nor reducing agent are.

b. $F^{\ominus}$ **d.** $Na^{\oplus}$ **g.** $Cl^{\ominus}$

9. **(3)** Balance the equation by any method.

$$4Zn + 10HNO_3 \longrightarrow 4\,Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

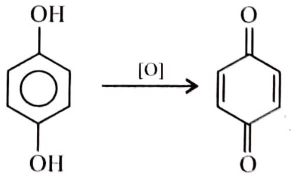
$$\therefore\ a + b + c = 4 + 3 + 1 = 8$$

10. **(3)** Balance the equation.

$$15H_2O + 3CN^{\ominus} \longrightarrow 3CO_2 + 3NO_3^{\ominus} + 30H^{\oplus} + 30e^-$$

$$\therefore\ \text{Number of } e^-\text{'s} = \frac{30}{10} = 3$$

11. **(4)**



$$[C_6H_5OH \longrightarrow C_6H_4O_2 + 4e^-\;]\ (n = 4)$$

$$6x = -4 \qquad\qquad 6x = 0$$

$$\uparrow\ 0 - (-4) = 4\ \uparrow$$

Archives

Main

ngle Correct Answer Type

1. (3) The half equations of the reaction are

$MnO_4^- \longrightarrow Mn^{2+}$

$C_2O_4^{2-} \longrightarrow CO_2$

The balanced half equations are

$MnO_4^- + 8H^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

On equating number of electrons, we get

$2MnO_4^- + 16H + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$

$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$

On adding both the equations, we get

$2MnO_4^- + 5C_2O_4^{2-} + 16H^- \longrightarrow 2Mn^{2+} + 2 \times 5CO_2$

$+ \frac{16}{2} H_2O$

$\therefore$ x, y and z are 2, 5 and 16 are respectively.

JEE Advanced

Single Correct Answer Type

1. **(4)** Haematite: $Fe_2O_3 \Rightarrow$ Oxidation state of Fe = III

Magnetite: $Fe_3O_4 \equiv FeO.\ Fe_2O_3$

Oxidation state of Fe = II, III

Multiple Correct Answers Type

1. **(2)**

A reducing agent loses electrons during redox reaction. Hence (B, D) is correct.

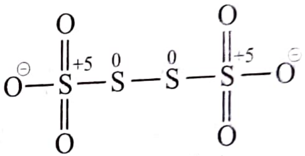
2. **(1, 2, 4)**

$$\underset{\text{(R.A.)}}{6I^{\ominus}} + \underset{\text{(O.A.)}}{ClO_3^{\ominus}} + 6H_2SO_4 \longrightarrow Cl^{\ominus} + 3I_2 + 3H_2O + 6HSO_4^{\ominus}$$

Numerical Value Type

1. **(5)**

$S_4O_6^{2-}$:



$$\overset{\ominus}{O}-\overset{+5}{S}(=O)_2-\overset{0}{S}-\overset{0}{S}-\overset{+5}{S}(=O)_2-\overset{\ominus}{O}$$

So difference in oxidation numbers of two types of S = (5 – 0) = 5

Chapter 3

Concept Application Exercises

Exercise 3.1

Subjective Type

1. $2H_2O + \cancel{4e} + O_2 \longrightarrow \cancel{2\overset{\ominus}{O}H} + \cancel{2\overset{\ominus}{O}H}] \times 5$

$2x = 0 \qquad 2x + 2 = -2$

$2x = -4$

$5\cancel{\overset{\ominus}{O}H} + NH_3 \longrightarrow NO + 5\cancel{e} + 4H_2O] \times 4$

$x + 3 = 0 \qquad x - 2 = 0$

$x = -3 \qquad x = 2$

$$5O_2 + 4NH_3 \longrightarrow 4NO + 6H_2O$$

When the same products are produced from a given set of reactants, the equation will be the same no matter what the medium is.

2. $\left(\overset{-4\ +3}{CN}\right)^{-1}$ or $CN^{\ominus} \longrightarrow CO_2 + NO_3^{\ominus}$

$C^{4-} + 2H_2O \longrightarrow CO_2 + 8e^- + 4H^{\oplus}$

$x = -4 \qquad x = 4$

$N^{3+} + 3H_2O \longrightarrow NO_3^{\ominus} + 2e^- + 6H^{\oplus}$

$x = 3 \qquad x = 5$

$$CN^{\ominus} + 5H_2O \longrightarrow CO_2 + 10H^{\oplus} + NO_3^{\ominus} + 10e^- \quad ...(i)$$

Reduction of $NO_3^{\ominus}$ to NO:

$4H^{\oplus} + 3e^- + NO_3^{\oplus} \longrightarrow NO + 2H_2O \quad ...(ii)$

$x - 6 = -1 \qquad x - 2 = 0$

$x = 5 \qquad x = 2$

Multiply Eq. (i) by 3 and Eq. (ii) by 10 and add them to get the final redox equation:

$$3CN^{\ominus} + 10H^{\oplus} + 7NO_3^{\oplus} \longrightarrow 3CO_2 + 10NO + 5H_2O$$

Acid ($H^{\oplus}$) and $CN^{\ominus}$ ion react to give HCN, a poisonous and deadly gas, unless the oxidising properties of the acid cause the oxidation of $CN^{\ominus}$ before the HCN can escape.

3. a. In $\overset{+3\ -1\times3}{Bi(OH)_3}$, Bi^{3+} is reduced to Bi and $\overset{+3}{Sn}O_2^{2-}$ (Stannite) is oxidised to $\overset{+4\,2-}{SnO_3}$ (Stannate)

$\overset{+3}{Bi} + \cancel{3e} \longrightarrow Bi] \times 2$

$2\overset{\ominus}{O}H + H_2O + \overset{+2}{Sn}O_2^{2-} \longrightarrow Sn^{+4}O_3^{2-} + \cancel{2e}$

$x = 2 \qquad x = 4$

$+ 2H_2O \times 3$

$$2Bi^{3+} + 6\overset{\ominus}{O}H + 3SnO_2^{2-} \longrightarrow 2Bi + 3SnO_3^{2-} + 3H_2O$$

or

$$2Bi(OH)_3 + 3SnO_2^{2-} \longrightarrow 2Bi + 3SnO_3^{2-} + 3H_2O$$

b. In $[\overset{+3}{Fe}(\overset{-1\times6}{CN})_6]^{3-}$, Fe^{3+} does not change, and $CN^{\ominus}$ is oxidised to CO_2 and $NO_3^{\ominus}$.

$30H_2O + [\overset{3+}{Fe}(\overset{-1\times6}{CN})_6]^{3-} \longrightarrow 6CO_2 + 6NO_3^{\ominus}$

$+ \cancel{60e^-} + Fe^{3+} + 60H^{\oplus} \quad ...(i)$

$14H^{\oplus} + \cancel{6e} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O \quad ...(ii)$

Multiply Eq. (ii) by 10 and add Eqs. (i) and (ii) to get final redox equation:

$$80H^{\oplus} + [Fe(CN)_6]^{3-} + 10Cr_2O_7^{2-} \longrightarrow 6CO_2 + 6NO_3^{\ominus} + Fe^{3+} + 20Cr^{3+} + 40H_2O$$

c. $33\overset{\ominus}{O}H + 17H_2O + 6V \longrightarrow HV_6O_{17}^{3-}$

$6x = 0 \qquad 1 + 6x - 34 = -3$

$6x = 30$

$+ 30e^- + 33H_2O$

or

$33\overset{\ominus}{O}H + 6V \longrightarrow HV_6O_{17}^{3-} + 16H_2O + \cancel{30e} \quad ...(i)$

$\cancel{2e} + 2H_2O \longrightarrow H_2 + 2\overset{\ominus}{O}H] \times 15 \quad ...(ii)$

$$3\overset{\ominus}{O}H + 14H_2O + 6V \longrightarrow HV_6O_{17}^{3-} + 15H_2$$

d. It is a disproportionation reaction.

$\cancel{2H^{\oplus}} + \cancel{2e} + P_2H_4 \longrightarrow 2PH_3] \times 3$

$2x + 4 = 0 \qquad 2x + 6 = 0$

$2x = -4 \qquad 2x = -6$

$2P_2H_4 \longrightarrow P_4H_2 + \cancel{6e} + 6H^{\oplus}$

$4x + 8 = 0 \qquad 4x + 2 = 0$

$4x = -8 \qquad 4x = -2$

$$5P_2H_4 \longrightarrow 6PH_3 + P_4H_2$$

e. $PO_4^{3-} \longrightarrow P_4$ and $C \rightarrow CO$

$32H^{\oplus} + \cancel{20e^-} + 4PO_4^{3-} \longrightarrow P_4 + 16H_2O \quad ...(i)$

$4x - 32 = -12 \qquad 4x = 0$

$4x = 20$

$H_2O + C \longrightarrow CO + \cancel{2e} + 2H^{\oplus}] \times 10 \quad ...(ii)$

$x = 0 \qquad x - 2 = 0$

$x = 2$

$$12H^{\oplus} + 10C + 4PO_4^{3-} \longrightarrow P_4 + 10CO + 6H_2O \quad ...(iii)$$

$\overset{+4}{Si}O_2$ to $\overset{+4}{Si}O_3^{2-}$, no change in oxidation state

$H_2O + SiO_2 \longrightarrow SiO_3^{2-} + 2H^{\oplus}$

or

$6H_2O + 6SiO_2 \longrightarrow 6SiO_3^{2-} + 12H^{\oplus} \quad ...(iv)$

Add Eqs. (iii) and (iv) to get the final redox equation.

$+10C + 4PO_4^{3-} + 6SiO_2 \longrightarrow P_4 + 10CO + 6SiO_3^{2-}$

To balance other ions, add $6Ca^{2+}$ to both sides.

$10C + 2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow P_4 + 10CO + 6CaSiO_3$

Exercise 3.2

Subjective Type

1. Reactions (a) to (d) are all disproportionation reactions

a. $2e^- + Br_2 \longrightarrow 2Br^{\ominus}$

$Br_2 \longrightarrow 2 \quad 2BrO_2^{\ominus} + 6e^-$

$2x = 0 \qquad 2x - 8 = -2$

$2x = 6$

(Mw of $Br_2 = 2 \times 80 = 160$)

$$Ew \text{ of } Br_2 = \left(\frac{Mw}{2} + \frac{Mw}{6}\right) = \left(\frac{160}{2} + \frac{160}{6}\right)$$
$$= 80 + 26.66 = 106.66$$

b. $$\overset{+1\ +1\ -2}{HCuCl_2} \longrightarrow Cu + Cu^{2+}$$
$$e^- + Cu^{\oplus} \longrightarrow Cu$$
$$Cu^{\oplus} \longrightarrow Cu^{2+} + e^-$$

Mw of $HCuCl_2 = 1 + 63.5 + 2 \times 35.5 = 135.5$

$$Ew \text{ of } HCuCl_2 = \left(\frac{Mw}{1} + \frac{Mw}{1}\right) = 135.5 + 135.5 = 271$$

c. $$2e^- + \overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+4}{Mn}O_2$$
$$\overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+7}{Mn}O_4^{\ominus} + e^-$$

(Mw of $MnO_4^{\ominus} = 55 + 4 \times 16 = 119$)

$$Ew \text{ of } MnO_4^{\ominus} = \left(\frac{Mw}{2} + \frac{Mw}{1}\right) = \left(\frac{119}{2} + \frac{119}{1}\right)$$
$$= 59.5 + 119 = 178.5$$

d. $$\overset{+5}{Cl}O_3^{\ominus} \longrightarrow Cl^{\ominus} + O_2$$

$3(-2 \rightarrow 0) = +6$

$5 - (-1) = 6$

Mw of $KClO_3 = 39 + 35.5 \times 16 \times 3 = 122.5$

$$Ew \text{ of } KClO_3 = \frac{Mw}{6} = \frac{122.5}{6} = 20.42$$

2. (1) i. Ew of $\overset{+2}{Fe}\left(\overset{+1}{H}C_2\overset{-2}{O_4}\right)_2^{-1 \times 2}$ as reducing agent.

Fe^{2+} is oxidised to Fe^{3+} and $2C_2O_4^{2-}$ to $4CO_2$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$2C_2O_4^{2-} \longrightarrow 4CO_2 + 4e^-$$

Mw of $Fe(HC_2O_4)_2$
$= 56 + 2(1 + 2 \times 12 + 4 \times 16) = 234$ g

$$\therefore\ Ew = \frac{234}{5} = 46.8 \text{ g}$$

Ew of $Fe(HC_2O_4)_2$ as an acid.
There are $2H^{\oplus}$

$$\therefore\ Ew = \frac{234}{2} = 117 \text{ g}$$

ii. Ew of $\overset{+3}{Fe}\left(\overset{+1}{H}C_2\overset{-2}{O_4}\right)_3^{-1 \times 3}$ as reducing agent.

Fe^{3+} does not oxidise only 3 $C_2O_4^{2-}$ is oxidised to $6CO_2$

$$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$$

Mw of $Fe(HC_2O_4)_3$
$= 56 + 3(1 + 2 \times 12 + 4 \times 16) = 323$ g

$$\therefore\ Ew = \frac{323}{6} = 53.83$$

Ew of $Fe(HC_2O_4)_3$ as an acid.
There are $3H^{\oplus}$

$$\therefore\ Ew = \frac{323}{3} = 107.6 \text{ g}$$

b. $2e^- + Cl_2 \longrightarrow 2Cl^{\ominus}$ (reduction)
Cl_2 can be oxidised either to $ClO^{\ominus}$ (in cold) or $ClO_3^{\ominus}$ (in hot). Since condition is not given, so check which is formed.

$$\underset{2x = 0}{Cl_2} \longrightarrow \underset{\substack{2x - 4 = -2 \\ 2x = 2}}{2ClO^{\ominus}} + 2e^-$$

$$Ew = \left(\frac{Mw}{2} + \frac{Mw}{2}\right) = \frac{71}{2} + \frac{71}{2} = 71 \text{ g}$$

or

$$\underset{2x = 0}{Cl_2} \longrightarrow \underset{\substack{2x - 12 = -2 \\ 2x = 10}}{2ClO_3^{\ominus}} + 10e^-$$

$$Ew = \left(\frac{Mw}{2} + \frac{Mw}{10}\right) = \frac{71}{2} + \frac{71}{10}$$
$$= 35.5 + 7.1 = 42.6$$

Given $Ew = 42.6$, so $ClO_3^{\ominus}$ is formed.

c. Mw of $K_2S_2O_3 = 2 \times 39 + 2 \times 32 + 3 \times 16 = 190$
In acidic medium

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \left(n = \frac{2}{2} = 1\right)$$

$$\therefore\ Ew = \frac{190}{1} = 190.0 \text{ g}$$

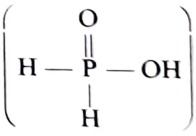
3. a. Mw of $H_3PO_2 = 3 \times 1 + 31 + 2 \times 16 = 66$

$$4e^- + \underset{\substack{3 + x - 4 = 0 \\ x = 1}}{H_3PO_2} \longrightarrow \underset{\substack{x + 3 = 0 \\ x = -3}}{PH_3}$$

$$\underset{x = 1}{H_3PO_2} \longrightarrow \underset{\substack{3 + x - 6 = 0 \\ x = 3}}{H_3PO_3} + 2e^-$$

$$\therefore Ew = \left(\frac{Mw}{4} + \frac{Mw}{2}\right) = Mw\left(\frac{1}{4} + \frac{1}{2}\right)$$
$$= \frac{3Mw}{4} = \frac{3}{4} \times 66 = 49.5$$

b. H_3PO_2 is monobasic acid



$\left(H - \overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}} - OH\right)$, so it gives one $H^{\oplus}$.

$$\therefore\ Ew = \frac{Mw}{1} = 66.$$

Exercise 3.3

Subjective Type

1. a. It is a redox reaction:

$$6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}\ (n = 6)$$

$$\left[\begin{array}{lll} Fe^{2+} & \longrightarrow & Fe^{3+} + e^- \\ \underset{\substack{2 + 4x - 16 = -2 \\ 4x = 12}}{2(HC_2O_4^{\ominus})} & \longrightarrow & \underset{\substack{4x - 16 = 10 \\ 4x = 16}}{4CO_2} + 4e^- \end{array}\right] (n = 5)$$

$Cr_2O_7^{2-} \equiv Fe(HC_2O_4)_2$
1 Eq $\equiv$ 1 Eq

$$\frac{1}{6}\text{ mol} = \frac{1}{5}\text{ mol}$$

$$1\text{ mol of Fe(HC}_2\text{O}_4)_2 = \frac{5}{6}\text{ mol of Cr}_2\text{O}_7^{2-}$$

b. It is a acid base reaction

NaOH ($n = 1$, one $\overset{\ominus}{\text{O}}\text{H}$ ion), $(\text{HC}_2\text{O}_4^{\ominus})_2$ ($n = 2$, 2H$^{\oplus}$ ions)

Fe^{2+} does not react with base (NaOH).

$$\text{NaOH} \equiv (\text{HC}_2\text{O}_4^{-1})_2$$

$$1\text{ Eq} \equiv 1\text{ Eq}$$

$$\frac{1}{1}\text{ mol} \equiv \frac{1}{2}\text{ mol}$$

$$2\text{ mol of NaOH} \equiv 1\text{ mol of Fe(HC}_2\text{O}_4)_2$$

2. In dilute basic medium, $\text{MnO}_4^{\ominus}$ is reduced to MnO_2.

$$3e^- + \text{MnO}_4^{\ominus} \longrightarrow \text{MnO}_2\ (n = 3),$$

$$\text{NO}_2^{\ominus} \longrightarrow \text{NO}_3^{\ominus} + 2e^-\ (n = 2)$$

$$\text{MnO}_4^{\ominus} \equiv \text{NO}_2^{\ominus}$$

$$1\text{ Eq} \equiv 1\text{ Eq}$$

$$\frac{1}{3}\text{ mol} \equiv \frac{1}{2}\text{ mol}$$

$$1\text{ mol of MnO}_4^{\ominus} \equiv \frac{3}{2}\text{ mol of NO}_2^{\ominus}$$

$$2\text{ mol of MnO}_4^{\ominus} = 3\text{ mol of NO}_2^{\ominus}$$

3. a. In strong basic medium, $\text{MnO}_4^{\ominus}$ is reduced to MnO_4^{2-}.

$$[e^- + \text{MnO}_4^{\ominus} \longrightarrow \text{MnO}_4^{2-}\ (n = 1)]$$

$$[\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^-\ (n = 2)]$$

In acidic medium, $\text{MnO}_4^{\ominus}$ is reduced to Mn^{2+}.

$$5e^- + \text{MnO}_4^{\ominus} \longrightarrow \text{Mn}^{2+}\ (n = 5)$$

$\text{MnO}_4^{\ominus}$ (acidic medium) $\equiv \text{C}_2\text{O}_4^{2-}$

$$1\text{ Eq} \equiv 1\text{ Eq}$$

$$\frac{1}{5}\text{ mol} \equiv \frac{1}{2}\text{ mol}$$

$1\text{ mol of C}_2\text{O}_4^{2-} \equiv \frac{2}{5}$ mol of $\text{MnO}_4^{\ominus}$ in acidic medium.

b. $\text{MnO}_4^{\ominus}$ (basic medium) $\equiv \text{C}_2\text{O}_4^{2-}$

$$1\text{ eq} \equiv 1\text{ eq}$$

$$\frac{1}{1}\text{ mol} \equiv \frac{1}{2}\text{ mol}$$

$1\text{ mol of C}_2\text{O}_4^{2-} = 2$ mol of $\text{MnO}_4^{\ominus}$ in basic medium

Ratio of $\text{MnO}_4^{\ominus}$ in acidic to basic medium

$$= \frac{2}{5} \div 2 = \frac{2}{5 \times 2} = \frac{1}{5} = 1{:}5$$

4. Fe(C$_2$O$_4$) is oxidised to Fe^{3+} and 2CO$_2$ by $\text{Cr}_2\text{O}_7^{2-}$ to 2Cr^{3+}.

$$\left.\begin{array}{l}\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^- \\ \text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^-\end{array}\right]\ n = 3$$

$$[6e^- + \text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+}\ (n = 6)]$$

In Fe$_2$(CrO$_4$)$_3$, Fe^{3+} is not oxidised, but $3\text{C}_2\text{O}_4^{2-}$ is oxidised to 6CO$_2$. (So $n = 6$)

$\text{Fe(C}_2\text{O}_4) \equiv \text{Cr}_2\text{O}_7^{2-}$	$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \equiv \text{Cr}_2\text{O}_7^{2-}$
$1\text{ Eq} \equiv 1\text{ Eq}$	$1\text{ Eq} \equiv 1\text{ Eq}$
$\frac{1}{3}\text{ mol} \equiv \frac{1}{6}\text{ mol}$	$\frac{1}{6}\text{ mol} \equiv \frac{1}{6}\text{ mol}$
$1\text{ mol of Cr}_2\text{O}_7^{2-}$	$1\text{ mol of Cr}_2\text{O}_7^{2-}$
$= \frac{6}{3} = 2\text{ mol of FeC}_2\text{O}_4$	$= 1\text{ mol of Fe}_2(\text{C}_2\text{O}_4)_3$

Ratio of mol of FeC$_2$O$_4$ and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 = \frac{2}{1} = 2:1$

5. Strength $= N \times Ew$ ($Mw = Ew$ of HCl = 36.5 g)

$$\text{N}_{\text{HCl}} = \frac{\text{Strength}}{Ew} = \frac{3.65}{36.5} = 0.1\text{ N}$$

$$\text{mEq of HCl} = N \times V(\text{mL}) = 0.1 \times 2000\text{ mL}$$
$$= 200\text{ mEq}$$

$$\text{HCl} \equiv \text{Al (OH)}_3$$

$$\text{mEq} \equiv \text{mEq}$$

$$200\text{ mEq} \equiv \frac{\text{Weight}}{Ew} \times 10^3$$

$$\left(\begin{array}{l}Mw\text{ of Al (OH)}_3 = 27 + 3 \times 17 = 78 \\ Ew = \frac{Mw}{3} = \frac{78}{3}\end{array}\right)$$

$$200 = \frac{\text{Weight} \times 10^3}{78/3}$$

$$\text{Weight of Al(OH)}_3 = \frac{200 \times 78}{1000 \times 3} = 5.2\text{ g} = 5200\text{ mg}$$

$$\text{Number of tablets of Al(OH)}_3 = \frac{5200}{520} = 10$$

6. Volume strength of $\text{H}_2\text{O}_2 = 5.6 \times N$

$$N_1\text{ of 2.8 vol H}_2\text{O}_2 = \frac{2.8}{5.6} = 0.5\text{ N}$$

$$N_2\text{ of 5.6 vol H}_2\text{O}_2 = \frac{5.6}{5.6} = 1\text{ N}$$

$$N_3\text{ of 22.4 vol H}_2\text{O}_2 = \frac{22.4}{5.6} = 4\text{ N}$$

$N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$ ($V_4 = 300 + 300 = 600$ mL)

$0.5 \times 100 + 1 \times 100 + 4 \times 100 = \text{N}_4 \times 600$

$$\therefore\ N_4 = \frac{50 + 100 + 400}{600} = \frac{550}{600} = 0.91\text{ N}$$

Volume strength = 5.6 × 0.91 = 5.09 vol

Alternatively :

$$\frac{(\text{Volume strength})_1 + (\text{Volume strength})_2 + (\text{Volume strength})_3}{6\text{ (Volume of solution diluted to 6 times)}}$$

$$= \frac{2.8 + 5.6 + 22.4}{6} = \frac{30.8}{6} = 5.1\text{ vol}$$

7. $\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}^{\ominus} \equiv \text{S}_2\text{O}_3^{2-}$

mEq≡ mEq≡ mEq≡ mEq

$$— \equiv — \equiv — \equiv 40\text{ mL} \times \frac{M}{20} \times 1\ (\text{‘}n\text{’ factor})$$

$$\equiv 2\text{ mEq} \equiv\ —\ \equiv 2\text{ mEq}$$

Thus mEq of Cl$_2$ in 20 mL of solution = 2 mEq

mEq of Cl_2 in 200 mL of solution $= \frac{2 \times 200}{20} = 20$ mEq.

Weight of Cl_2 = mEq × 10^{-3} × Ew of Cl_2

$$= 20 \times 10^{-3} \times \frac{71}{2} \left(\underset{(n = 2)}{Cl_2 + 2e^-} \longrightarrow 2e^- \right)$$

$= 0.71$ g

$$\text{\% of available } Cl_2 = \frac{\text{Weight of } Cl_2 \times 100}{\text{Weight of } CaOCl_2}$$

$$= \frac{0.71 \times 100}{10} = 7.1\%$$

Exercise 3.4
Subjective Type

1. Eq of HCl $= \frac{0.25 \times 30}{1000}$

Let x g of K_2CO_3 and $(0.5 - x)$ g of Li_2CO_3 reacts.

Eq of $K_2CO_3 = \frac{x}{69}$, Eq of $Li_2CO_3 = \frac{0.5 - x}{37}$

$$\therefore \frac{x}{60} + \frac{0.5 - x}{37} = \frac{0.25 \times 30}{1000} \Rightarrow x = 0.48 \text{ g}$$

% of $K_2CO_3 = \frac{0.48}{0.5} \times 100 = 96\%$

% of $Li_2CO_3 = 4\%$

2. a. 90% H_2SO_4 Weight/Volume ⇒ 90 g/100 mL

⇒ Mass/L = 900 g

Mass of solution/L = 1000 × 1.47 = 1470 g

⇒ Mass of H_2O = 1470 – 900 = 570 g

$$m = \frac{900/98}{570} \times 1000 = 16.11$$

3. x mol each of $NaHCO_3$ and Na_2CO_3

⇒ $84x + 106x = 1.9$ g (given)

$x = 0.01$

⇒ millimol of each = 10

Now, mEq of H_2SO_4 = mEq of $(NaHCO_3 + Na_2CO_3)$

$2 \times 0.25 \times V = 1 \times 10 + 2 \times 10$

⇒ $V = 60$ mL

Exercise 3.5
Subjective Type

1. $N_1(KMnO_4) = 3/31.6$

$N_2(H_2O_2) = 2/17 = 0.1176$

$N_1V_1 = N_2V_2$

$$V_1 = \frac{0.1176 \times 20 \times 31.6}{3} = 24.78 \text{ mL}$$

1 NH_2O_2 = 5.6 volume of O_2

0.1176 N of H_2O_2 = 5.6 × 0.1176 = 0.66 V

2. $N_A = 25/10 = 2.5$ N

$N_B = 25/40 = 0.625$ N

Let V is the volume for solution of N_A and for the solution B volume is $(1 - V)$ L.

$\therefore$ $2.5V + 0.625(1 - V) = 1$ equivalent of acid

$\therefore$ $V = 0.2$ L

$V_A = 200$ mL, $V_B = 800$ mL

3. Total HCl $= \frac{44.4 \times 0.5}{1000} \approx 0.0222$ eq.

$$M_2CO_3 + 2HCl \longrightarrow 2MCl + H_2O + CO_2$$

2 Eq of HCl = 1 mol of CO_3^{2-}

0.0222 Eq of HCl $= \frac{0.0222}{2} = 0.0111$ mol of total CO_3^{2-}

Since moles are equal, therefore, the number of moles of M_2CO_3 is equal to the number of moles of M'_2CO_3 i.e., 0.0111/2 moles of each metal carbonate is required.

Molecular weight of $M_2CO_3 = 2 \times 7 + 60 = 74$

Molecular weight of $M'_2CO_3 = (2x + 60)$

Weight of $M_2CO_3 = \frac{74 \times 0.0111}{2}$

Weight of $M'_2CO_3 = (2x + 60) \times \frac{0.0111}{2}$

$$\therefore \frac{74 \times 0.0111}{2} + \frac{(2x + 60) \times 0.0111}{2} = 1.0 \text{ g (given)}$$

$\therefore$ $x = 23.09$

Atomic weight of the other metal = 23.09

For the formation of sulphates:

$$M_2CO_3 + H_2SO_4 \longrightarrow M_2SO_4 + H_2O + CO_2$$

0.0111/2 mol of M_2CO_3 = 0.0111/2 mol of sulphate

Total weight of sulphates

$$\frac{0.0111 \times 110}{2} + \frac{0.0111 \times 142.18}{2} = 1.4 \text{ g}$$

4. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

Total acid used $= 230 \times \frac{N}{10}$ HCl = 23 mEq HCl

Excess acid = 40 mL $\frac{N}{10}$ NaOH = 4 mEq of acid

Acid used = 23 – 4 = 19 mEq of acid

= 19 mEq of $CaCO_3$

$= 19 \times 10^{-3} \times 50 = 0.95$ g

% of $CaCO_3 = \frac{0.95}{1} \times 100 = 95\%$

5. 1 mole of CO = 28 g, 1 mole of I_2 = 253.8 g

5 mole of CO = 1 mole of I_2

Moles of $I_2 = \frac{0.2}{253.8}$

$$\therefore \frac{0.2}{253.8} \text{ moles of } I_2 = \frac{5 \times 0.2}{253.8} \times 28 \text{ g of CO}$$

= 0.110 g of CO

6. The reaction between KIO_3 and KI is

$$KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3H_2O + 3I_2$$

The reaction of I_2 with thiosulphate ion is

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^{\ominus}$$

From these reactions, we can write

1 mol $KIO_3 \equiv 3$ mol I_2

1 mol $I_2 \equiv 2$ mol $S_2O_3^{2-}$

From the given mass of KIO_3, we get

$$\text{Amount of } KIO_3 = \frac{0.10\text{ g}}{214.0\text{ g mol}^{-1}} = 4.6729 \times 10^{-4}\text{ mol}$$

Amount of I_2 generated $= 3 \times 4.6729 \times 10^{-4}$ mol

Amount of $S_2O_3^{2-}$ consumed $= 2(3 \times 4.6729 \times 10^{-4}$ mol) ...(i)

Let m be the molality of thiosulphate solution.

From the given volume of thiosulphate solution, we get

Amount of $S_2O_3^{2-}$ consumed $= MV = M(45.0 \times 10^{-3}\text{ L})$ ...(ii)

Equating Eqs. (i) and (ii), we get

$M(45.0 \times 10^{-3}\text{ L}) = 2(3 \times 4.6729 \times 10^{-4}\text{ mol})$

$$M = \frac{2(3 \times 4.6729 \times 10^{-4}\text{ mol})}{45.0 \times 10^{-3}\text{ L}} = 0.0623\text{ mol L}^{-1}$$

Exercise 3.6

Subjective Type

1. **With phenolphthalein**

mEq of HCl used for 200 mL solution $= 17.5 \times 0.1 \times 1$

$= 1.75$

Let a and b mEq of NaOH and Na_2CO_3, respectively.

$$a + \frac{b}{2} = 1.75 \quad \text{...(i)}$$

With methyl orange indicator

mEq of HCl used for solution after first end point

$= 2.5 \times 0.1 \times 1 = 0.25$

$$\frac{b}{2} = 0.25 \quad \text{...(ii)}$$

By Eqs. (i) and (ii)

a (mEq of NaOH) $= 1.5$

Weight of NaOH $= 1.5 \times 10^{-3} \times 40$

$= 0.06$ g/200 mL

b (mEq of Na_2CO_3) $= 0.5$

$$\text{Weight of } Na_2CO_3 = 0.5 \times 10^{-3} \times \frac{106}{2}$$

$= 0.0265$ g/200 mL

2. **With phenolphthalein indicator**

mEq of H_2SO_4 used $= 12 \times 0.05 \times 2$ (n-factor)

$= 1.2$

Let a and b mEq of $NaHCO_3$ and Na_2CO_3, respectively.

$$\therefore \frac{b}{2} = 1.2 \quad \text{...(i)}$$

With methyl orange indicator

mEq of H_2SO_4 used from the beginning $= 40 \times 0.05 \times 2$

$= 4.0$

$a + b = 4.0$ ...(ii)

By Eqs. (i) and (ii), we get

a (mEq of $NaHCO_3$) $= 1.6$

Weight of $NaHCO_3 = 1.6 \times 10^{-3} \times 84$

$= 0.1344$ g/30 mL

$$= \frac{0.1344 \times 1000}{30}\text{ g L}^{-1}$$

$= 4.48$ g L^{-1}

b (mEq of Na_2CO_3) $= 2.4$

$$\text{Weight of } Na_2CO_3 = 2.4 \times 10^{-3} \times \frac{106}{2}$$

$= 0.1272$ g/30 mL

$$= \frac{0.1272 \times 1000}{30}\text{ g L}^{-1}$$

$= 4.24$ g L^{-1}

3. $$CH_3(CH_2)_nCOOH + \left[\frac{3n+4}{2}\right]O_2 \longrightarrow (n+2)\,CO_2 + \left[\frac{2n+4}{2}\right]H_2O$$

1 mol of acid $= (n + 2)$ mol of CO_2

$$\frac{0.58}{(60+14n)}\text{ mol of acid} = \frac{(n+2) \times 0.58}{(60+14n)}\text{ mol of } CO_2$$

This CO_2 is passed in excess NaOH where CO_2 is converted to Na_2CO_3 and some NaOH is left

With phenolphthalein:

$\frac{1}{2}$ mEq of Na_2CO_3 + mEq of NaOH left = mEq of HCl

(Let a mEq) (Let b mEq) $= 50 \times 1 \times 1$

$= 50$

i.e., $$\frac{a}{2} + b = 50 \quad \text{...(i)}$$

With methyl orange

$$a + b = 80 \times 1 \times 1 \quad \text{...(ii)}$$

By Eqs. (i) and (ii), we get

b (mEq of NaOH left) $= 20$

a (mEq of Na_2CO_3 formed) $= 80 - 20 = 60$

Total mEq of NaOH used $= 20 + 60 = 80$

Weight of NaOH (total) $= 80 \times 10^{-3} \times 40 = 3.2$ g

Also, mEq of Na_2CO_3 = mEq of CO_2

$$60 = \frac{(n+2) \times 0.58}{(60+14n)} \times 2\ (n\text{ factor}) \times 10^3$$

$\therefore n = 4$

4. **a.** At the end point:

mEq of HCl = mEq of NaOH

$40 \times N = 0.1 \times 1 \times 32.56$

$N_{HCl} = 0.0814$

b. mEq of HCl $= 0.0814 \times 40 = 3.256$

mEq of NaOH added $= 30 \times 0.1 = 3.0$

mEq of HCl left $= 3.256 - 3.0 = 0.256$

$$N_{HCl} = \frac{\text{mEq of HCl}}{\text{Total volume}} = \frac{0.256}{30 + 40}$$

$= 3.66 \times 10^{-3}$

$\therefore N_{HCl} = 3.66 \times 10^{-3}$

c. $pH = -\log [H^{\oplus}] = -\log (3.66 \times 10^{-3}) = 2.4365$

d. At the end point, pH = 7.

5. Let a, b, and c be the mEq of Na_2CO_3, $NaHCO_3$, and NaOH, respectively.

a. **With phenolphthalein:**

$$\text{mEq of NaOH} + \frac{1}{2}\text{mEq of } Na_2CO_3 = \text{mEq of HCl}$$

$$\frac{1}{40} \times 10^3 + \frac{1}{2} \times \frac{1}{53} \times 10^3 = 1 \times V_1$$

$$\therefore \quad V_1 = 34.4 \text{ mL}$$

b. **With methyl orange from the beginning:**

$$\text{mEq of NaOH} + \text{mEq of } Na_2CO_3 + \text{mEq of } NaHCO_3 = \text{mEq of HCl}$$

$$\frac{1}{40} \times 10^3 + \frac{1}{53} \times 10^3 + \frac{1}{84} \times 10^3 = 1 \times V_2$$

$$\therefore V_2 = 55.8 \text{ mL}$$

c. **With methyl orange when first end point using phenolphthalein is used:**

$$\frac{1}{2}\text{ mEq of } Na_2CO_3 + \text{mEq of } NaHCO_3 = \text{mEq of HCl}$$

$$\frac{1}{2} \times \frac{1}{53} \times 10^3 + \frac{1}{84} \times 10^3 = 1 \times V_3$$

$$\therefore V_3 = 21.3 \text{ mL}$$

6. Total +ve charge = Total –ve charge

$$A_x^{2+} (CO_3^{2-})y \left(\overset{\ominus}{O}H\right)_z : 2x = 2y + z \quad \text{...(i)}$$

H_2SO_4 reacts with CO_3^{2-} and $\overset{\ominus}{OH}$ ions of the salt.

With phenolphthalein:

Half of the salt is neutralised as carbonate is converted to $HCO_3^{\ominus}$ (bicarbonate ion) and $\overset{\ominus}{OH}$ ions are completely neutralised.

$$\therefore \begin{pmatrix}\text{mEq of } H_2SO_4 \\ \text{in 100 mL of solution}\end{pmatrix}$$

$$= \frac{1}{2}\text{ mEq of salt for } CO_3^{2-} + \text{mEq of salt for } \overset{\ominus}{OH}$$

$$\frac{10 \times 1 \times 100}{50} = \frac{1}{2} \times \frac{1.7225 \times 10^3}{M/2y} + \frac{1.7225 \times 10^3}{M/z}$$

$$20 = \frac{1722.5 \times y}{M} + \frac{1722.5 \times z}{M} \quad \text{...(ii)}$$

With methyl orange:

Salt is completely neutralised.

$$\begin{bmatrix}\text{mEq of } H_2SO_4 \\ \text{in 100 mL of sol}\end{bmatrix}$$

$$= \text{mEq of salt for } CO_3^{2-} + \text{mEq of salt for } \overset{\ominus}{OH}$$

$$\frac{15 \times 1 \times 100}{50} = \frac{1.7225 \times 10^3}{M/2y} + \frac{1.7225 \times 10^3}{M/z}$$

$$30 = \frac{1722.5 \times 2y}{M} + \frac{1722.5 \times z}{M} \quad \text{...(iii)}$$

Subtracting Eq. (ii) from Eq. (iii), we get

$$10 = \frac{1722.5y}{M} \quad \text{...(iv)}$$

By Eqs. (ii) and (iv), we get

$$10 = \frac{1722.5z}{M} \quad \text{...(v)}$$

By Eqs. (iv) and (v), we get

$$y = z \quad \text{...(vi)}$$

Also, from Eqs. (i) and (vi), we get

$x = 1.5y$

Thus, for simplest ratio

$x : y : z :: 1.5 : 1 : 1$ or $3 : 2 : 2$.

Therefore, formula of salt is: $A_3(CO_3)_2(OH)_2$

Exercise 3.7

1. $MgCl_2 = \dfrac{10 \times 100}{65} = 10.53$ ppm,

$CaSO_4 = \dfrac{8 \times 100}{136} = 5.92$ ppm

ppm of $CaCO_3 = 10.53 + 5.92 = 16.45$ ppm.

2. a. $$\underset{1\text{ mol}}{Ca(HCO_3)_3} + \underset{1\text{ mol}}{Ca(OH)_2} \longrightarrow 2CaCO_3 + 2H_2O$$

b. $$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + \cancel{MgCO_3} + 2H_2O$$

$$\cancel{MgCO_3} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3$$

$$\underset{1\text{ mol}}{Mg(HCO_3)_2} + \underset{2\text{ mol}}{2Ca(OH)_2} \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

[*Mw* of $Ca(HCO_3)_3$, $Mg(HCO_3)_2$, and $Ca(OH)_2$, respectively, are: 162, 146, and 74 g mol^{-1}]

From reaction (a),

Weight of $Ca(OH)_2 = \dfrac{74 \times 7.5}{162} = 3.42$ g

From reaction (b),

Weight of $Ca(OH)_2 = \dfrac{2 \times 74 \times 5.0}{146} = 5.06$ g

Total weight of $Ca(OH)_2$ in 1 L of $H_2O = 3.42 + 5.06 = 8.48$ g L^{-1}

Weight of $Ca(OH)_2$ in 10^3L $= 8.48 \times 10^3$ g

3. 5 mL of N/20 $Na_2CO_3 = \dfrac{5 \times 50}{20 \times 1000}$ g $CaCO_3$

So, 200 parts of water contains $= \dfrac{5 \times 50}{20 \times 1000}$ parts of $CaCO_3$ equivalent

10^6 parts of water contains $= \dfrac{5 \times 50 \times 10^6}{20 \times 1000 \times 200}$

$= 62.5$ ppm

Therefore, hardness = 62.5 ppm

Exercises

Single Correct Answer Type

1. (1) $N = \dfrac{W_2 \times 1000}{Ew_2 \times V_{\text{mL}}}$

$N = \dfrac{34 \times 1000}{17 \times 1120} = \dfrac{200}{112}$

1 N of H_2O_2 = 5.6 volume strength

$\dfrac{200}{112}$ N of $H_2O_2 = 5.6 \times \dfrac{200}{112} = 10\ V$

2. (4) $H_2O_2 \equiv KI \equiv I_2$

mEq of $H_2O_2 = 5 \times N$

$$\text{mEq of } I_2 = \frac{\text{Weight}}{Ew} \times 1000$$

$$= \frac{1.27}{127} \times 1000 = 10 \text{ mEq}$$

$I_2 = Mw = 254$

$Ew = \dfrac{Mw}{2} = \dfrac{254}{2} = 127$

$\therefore$ mEq of H_2O_2 = mEq of I_2

$5 \times N = 10 \quad \therefore \quad N = 2$

1 N of H_2O_2 = 1.7% H_2O_2

2 N of H_2O_2 = 3.4% H_2O_2

3. (1) In Q.2, (above), N of $H_2O_2 = 2$

$\therefore$ 1 N of H_2O_2 = 5.6 volume strength

2 N of H_2O_2 = 11.2 volume strength

4. (1) $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow 2Cr^{3+} + Fe^{3+}$

i. $6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}\ (x = 6)$

ii. $Fe^{2+} \longrightarrow Fe^{3+} + e^-\ (x = 1)$

mEq of $Cr_2O_7^{2-}$ = mEq of Fe^{2+}

$20 \times 0.1 \times 6$ mEq $= 10 \times N$

$N = 1.2$

$M = \dfrac{N}{n\text{ 'factor'}} = \dfrac{1.2}{1} = 1.2$ M

5. (4) Ore of Mn is MnO_2 (pyrolusite).

$2e^- + MnO_2 \longrightarrow Mn^{2+}$

$(x = 4) \longrightarrow x = +2 (x = 4 - 2 = 2)$

Ew of $MnO_2 = \dfrac{Mw}{2}$

Excess of $C_2O_4^{2-} = 18.28 \times 0.1232 \times 5$ mEq of MnO_4^-

or $= 11.26$ mEq of $C_2O_4^{2-}$

Total $C_2O_4^{2-} = 50 \times 0.2750 \times 2$ mEq $= 27.5$ mEq

Reacted $C_2O_4^{2-} = 27.5 - 11.26 = 16.24$

$= 16.24$ mEq of $C_2O_4^{2-}$

or $= 16.24$ mEq of MnO_2

$= 16.24 \times 10^{-3}$ eq of MnO_2

Moles of $MnO_2 = \dfrac{16.24 \times 10^{-3}}{2}$

$= 8.12 \times 10^{-3}$ mol

6. (3) mEq of $\overset{\ominus}{O}H = 20 \times 0.1 \times 2 = 4$ mEq

mEq of $HClO_4$ $(x = 1) = 10 \times 0.2 \times 1 = 2$ mEq

mEq of $\overset{\ominus}{O}H$ left $= 4 - 2 = 2$ mEq

Concentration or N of $\overset{\ominus}{O}H = \dfrac{2 \text{ mEq}}{30 \text{ mL}}$

$= 0.066$ N of $\overset{\ominus}{O}H$

$= 0.066$ M of $\overset{\ominus}{O}H$

7. (3) $\underset{x=6}{3e^- + CrO_4^{2-}} \longrightarrow \underset{x=3}{[Cr(OH)_4]^{\ominus}}$

$(x = 6 - 3 = 3)$

$\therefore Ew = \dfrac{Mw}{3}$

8. (4) Concentration of $H^{\oplus}$ in 1 mL $= 10^{-5}$ M

Concentration of $H^{\oplus}$ in 1000 mL $= 10^{-8}$ M,

(pH = 6.98)

9. (1) mEq of $KMnO_4 = V \times 0.1 \times 5$

mEq of $Fe(C_2O_4)_2 = \dfrac{\text{Weight in g}}{Ew} \times 1000$

$$\left[\begin{array}{l} Fe^{+2} \longrightarrow Fe^{+3} + e^- \\ C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \end{array}\right] \quad (n = 3)$$

Ew of $Fe(C_2O_4) = \dfrac{Mw}{3} = \dfrac{144}{3}$

$\therefore$ mEq of $Fe(C_2O_4) = \dfrac{5 \times 10^{-3}}{\frac{144}{3}} \times 10^3 = \dfrac{5 \times 3}{144}$

$\therefore$ mEq of $KMnO_4$ = mEq of $Fe(C_2O_4)$

$\therefore V \times 0.1 \times 5 = \dfrac{5 \times 3}{144}$

$\therefore V = 0.20$ mL

10. (3) $\underset{x=+n}{A^{n+}} \longrightarrow \underset{x-6=-}{AO_3^-}$ (undergoes oxidation) $\therefore x = 5$

$\therefore$ Number of e^- released in oxidation $= (5 - n)$

$\therefore$ Equivalents of $MnO_4^{\ominus} = 4 \times (5 - n)$

Equivalents of $MnO_4^{\ominus} = 1.6 \times 5$

$\therefore 4 \times (5 - n) = 1.6 \times 5$

$\therefore n = 3$

11. (3) $\underset{2x+4=0}{N_2H_4} \longrightarrow \underset{(2y)}{2N} + 10e^-$

$2x = -4$

$\therefore 2y - (-4) = 10$

$y = 3$

12. (1)

$$O_3 \longrightarrow O_2 + O \quad \text{...(i)}$$

$$H_2O_2 \longrightarrow H_2O + O \quad \text{...(ii)}$$

$$\underset{1/2 \text{ vol}}{O} + \underset{1/2 \text{ vol}}{O} \longrightarrow \underset{1 \text{ vol}}{O_2} \quad \text{...(iii)}$$

From Eqs. (i) and (ii), we infer that 100 mL of O_3 at STP will produce 100 mL of molecular O_2 as such and

100 mL of oxygen molecule after reaction with H_2O_2. This new volume of 100 mL of molecular oxygen after reaction with H_2O_2 is contributed equally by O_3 and H_2O_2. Thus, 50 mL of oxygen have been contributed by H_2O_2.

Again, we know

Volume of H_2O_2 × Volume strength of H_2O_2

$$= \text{Volume of } O_2 \text{ at STP}$$

$\therefore$ 100 mL of '10 *V*' $H_2O_2 \equiv$ 1000 mL of O_2 at STP

After utilisation of 50 mL of O_2, according to Eq. (iii), the balance (1000 – 50) = 950 mL of O_2 at STP are still retainable by 100 mL of H_2O_2.

Hence volume strength of H_2O_2 after reaction

$$= \frac{\text{Volume of } O_2 \text{ at STP}}{\text{Volume of } H_2O_2} = \frac{950}{100} = 9.5 \text{ V}$$

$\therefore$ Volume strength = 9.5

13. **(2)** Volume of O_2 at STP = 10 mL × 10 'V' = 100 mL

22400 mL of O_2 at STP = 1 mol = 4 Eq

$$100 \text{ mL of } O_2 \text{ at STP} = \frac{4}{22400} \times 100 = \frac{1}{56} \text{ Eq}$$

Eq of $KMnO_4$ = Eq of O_2

$$= \frac{1}{56} \text{ Eq of } KMnO_4$$

$$= \frac{1}{56} \times 31.5 \text{ g of } KMnO_4$$

$$= 0.564 \text{ g}$$

$\left(Ew \text{ of } KMnO_4 \text{ in acidic medium} = \frac{Mw}{5} = 31.5\right)$

Alternate method:

N of '10 *V*' of H_2O_2:

5.6 '*V*' of H_2O_2 = 1N

$$10 \text{ '}V\text{' of } H_2O_2 = \frac{10}{5.6} \text{ N}$$

mEq of $KMnO_4$ = 100 × N

$\therefore$ mEq of H_2O_2 = mEq of $KMnO_4$

$$\frac{100}{5.6} = 100 \times \text{N} \Rightarrow \text{N} = \frac{1}{5.6}$$

$$\text{Strength of } KMnO_4 = N \times Ew = \frac{1}{5.6} \times 31.5$$

$$= 5.64 \text{ g L}^{-1}$$

5.64 g of $KMnO_4 \Rightarrow$ 1000 mL

$\therefore$ In 100 mL of $KMnO_4$, the amount of $KMnO_4$ = 0.564 g

14. **(4)**

Distilled H_2O	Tap H_2O	Boiled H_2O
[No hardness]	[Temporary+ permanent hardness]	[Only permanent hardness]
(Volume of soaps solution)		
1 mL	13 mL	5 mL

Volume of soap solution used effectively in tap water = 13 – 1 = 12 mL

$\therefore$ Temporary + Permanent hardness = 12 mL

Volume of soap solution used effectively in boiled water = 5 – 1 = 4 mL

Permanent hardness = 4 mL

$\therefore$ Temporary + Permanent hardness = 12 mL

Permanent hardness = 4 mL

Temporary hardness = 8 mL

$$\therefore \frac{\text{Temporary hardness}}{\text{Permanent hardness}} = \frac{8}{4} = 2:1$$

15. **(2)** 100 g of H_2O_2 sample solution contains *x* g of H_2O_2.

$$3.4 \text{ g of solution contains} = \frac{x}{100} \times 3.4$$

$$\text{Weight of } H_2O_2 = \frac{3.4\,x}{100}$$

$$\text{Eq of } H_2O_2 = \frac{3.4\,x}{100} \times \frac{1}{17}$$

$$\text{mEq of } H_2O_2 = \frac{3.4\,x}{100 \times 17} \times 1000 = \frac{34x}{17} = 2x$$

mEq of $KMnO_4 = x \times N$

$\therefore \quad x \times N = 2x$

$N = 2$

16. **(1)** Volume of O_2 at STP = 100 mL × 11.2 volume strength

= 1120 mL of O_2 at STP

(Since 1 N = 5.6 volume strength ; 2 N = 11.2 volume strength of H_2O_2)

Volume of O_2 produced by H_2O_2 = 1120 mL

Same volume of O_2 will be produced by $KMnO_4$ = 1120 mL

Total volume of O_2 = 2240 mL = 2.24 L

17. **(2)**

i.

$$3e^- + \underset{\substack{x-8=-2 \\ x=6}}{CrO_4^{2-}} \longrightarrow \underset{\substack{x-4=-1 \\ x=3}}{[Cr(OH)_4]^{\ominus}}$$

$$Ew \text{ of } CrO_4^{2-} = \frac{Mw}{3}$$

ii.

$$\underset{\substack{2x-6=-2 \\ 2x=4}}{S_2O_3^{2-}} \longrightarrow \underset{\substack{2x-6=-4 \\ 2x=12}}{2SO_4^{2-}} + 8e^-$$

$$Ew \text{ of } S_2O_3^{2-} = \frac{Mw}{8}$$

$N_1V_1\,(CrO_4^{2-}) = N_2V_2\,(S_2O_3^{2-})$

i.e., mEq of CrO_4^{2-} = mEq of $S_2O_3^{2-}$

$V_1 \times 0.2 \times 3 = 30 \times 0.2 \times 8$

$$V_1 = \frac{30 \times 0.2 \times 8}{0.2 \times 3} = 80 \text{ mL}$$

18. **(4)** Maximum capacity = $300 \times \frac{6}{5} = 360$ mL

If volume is more than 360, it will burst.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{300}{300} = \frac{360}{T_2}$$

$T_2 = 360\text{ K} = 360 - 273 = 87°\text{C}$

19. **(3)** FeC_2O_4 m $Fe^{2+} + C_2O_4^{2-}$

$MnO_4^{\ominus}$ oxidises Fe^{2+} and $C_2O_4^{2-}$ both.

$Fe^{2+} + C_2O_4^{2-} \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$

$MnO_4^{\ominus} + 5e^- \longrightarrow Mn^{2+}$

$5FeC_2O_4 \equiv 3\ MnO_4^{\ominus}$

$1\ FeC_2O_4 \equiv \frac{3}{5}\ MnO_4^{\ominus}$

20. **(2)** $\underset{1+x-6=0,\ x=5}{HNO_3^{\ominus}} + 4e^- \longrightarrow \frac{1}{2}\underset{a}{\overset{+1\times2\ -2}{N_2O}}$ (Species with oxidation number = +1 is N_2O)

Change in oxidation number $= 5 - a = 4 \Rightarrow a = 1$

21. **(2)** $5Fe^{2+}\ MnO_4^{\ominus} + 8H^{\oplus} \longrightarrow 5Fe^{3+} + 4H_2O + Mn^{2+}$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^{\oplus} \longrightarrow 6Fe^{3+} + 7H_2O + 2Cr^{3+}$

22. **(4)** $SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

$$\left.\begin{array}{l} H_2SO_4 \equiv 2NaOH \\ 2HCl \equiv 2NaOH \end{array}\right] = 4\ NaOH$$

23. **(2)** $MnO_4^{\ominus} + 5e^- \longrightarrow Mn^{2+}$ (acidic)

$MnO_4^{\ominus} + 3e^- \longrightarrow MnO_2$ (basic)

$100\text{ mL } H_2O_2 \equiv 100 \times 5\text{ N } MnO_4^{\ominus} \equiv V \times 3\text{ N } MnO_2$

$V = \frac{500}{3}\text{ mL}$

24. **(4)** $10 \times N_1\ (H_2O_2) \equiv 10 \times \frac{N}{0.56}\ MnO_4^{\ominus}$

$N_1\ (H_2O_2) = \frac{1}{0.56}$

'x volume' H_2O_2 has normality $= \frac{x}{5.6}$

$\frac{x}{5.6} = \frac{1}{0.56} \Rightarrow x = 10$

25. **(3)** $I^{\ominus}$ is limiting reagent, so one mole $I^{\ominus}$ will give $\frac{1}{4}$ mol or 0.25 mole of HgI_4^{2-}.

26. **(1)** **i.** With phenolphthalein indicator, $NaHCO_3$ does not react with HCl whereas with Na_2CO_3 is 50% reaction.

$V_{HCl} = x$ mL (Half titre value of Na_2CO_3)

ii. With methyl orange indicator, $NaHCO_3$ reacts completely with HCl and with Na_2CO_3 is 100% reaction.

But y mL of HCl is added after Na_2CO_3 has reacted upto $NaHCO_3$ i.e., half titre value of Na_2CO_3.

V_{HCl} = Full litre value of $NaHCO_3$ + Half titre value of Na_2CO_3

$y\text{ mL} = x' + x\text{ mL}$

∴ Volume of HCl required for complete reaction of $Na_2CO_3 = x\text{ mL} + x\text{ mL} = 2x\text{ mL}$

27. **(1)** **i.** $MnO_4^{\ominus} \longrightarrow Mn^{2+}$ (acidic) $Ew = \frac{Mw}{5}$

ii. $MnO_4^{\ominus} \longrightarrow MnO_2$ (neutral) $Ew = \frac{Mw}{3}$

iii. $MnO_4^{\ominus} \longrightarrow MnO_4^{2-}$ (basic) $Ew = \frac{Mw}{1}$

Ratio is $\frac{1}{5} : \frac{1}{3} : \frac{1}{1} = 3:5:15$

28. **(1)** $2NH_3 + OCl^{\ominus} \longrightarrow N_2H_4 + Cl^{\ominus} + H_2O$

29. **(3)** $SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^{\oplus} + 2e^-$

mEq of salt = mEq of SO_3^{2-}

$\Rightarrow (0.1 \times n) \times 50 \equiv (0.1 \times 2) \times 25$

$\Rightarrow n = 1$

$M^{3+} + e^- \longrightarrow M^{2+}$

30. **(3)** 20 mL of x M HCl ≡ 10 mL of 0.1 M $NaHCO_3$ + 5 mL of 0.2 M Na_2CO_3

(methyl orange indicated 100% reaction of $NaHCO_3$ and Na_2CO_3)

0.2 M Na_2CO_3 = 0.4 Na_2CO_3

$20x = 1 + 2 \Rightarrow x = 0.15$

31. **(3)** 1 N = 5.6 vol

⇒ Normalities of two solutions are 1 N and 2 N.

Normality of mixture $= \frac{1 \times 1 + 1 \times 2}{1 + 1} = \frac{3}{2} = 1.5\text{ N}$

Volume strength $= \frac{3}{2} \times 5.6 = \frac{16.8}{2} = 8.4$ vol

32. **(1)** pH = 2, $[H^{\oplus}] = 10^{-2}$ M

$$[Ca^{2+}] = \frac{10^{-2}}{2} = 0.5 \times 10^{-2} \times 40\text{ g L}^{-1}$$

$$= \frac{0.5 \times 10^{-2} \times 40 \times 10^{6}}{10^{3}}\text{ g}/10^{6}\text{mL} = 200\text{ ppm}$$

33. **(4)** $100 \times 5\text{ N }(MnO_4^{\ominus}) \equiv V \times 3\text{ N }(MnO_4^{\ominus})$

$V = \frac{500}{3}\text{ mL}$

34. **(3)** $K_2\overset{+4}{Mn}F_6 \rightleftharpoons \overset{+4}{Mn}F_4 + 2KF$ ...(i)

$2KF + 2SbF_5 \longrightarrow 2KSbF_6$ ...(ii)

$\overset{+4}{Mn}F_4 \rightleftharpoons \overset{+3}{Mn}F_3 + \frac{1}{2}F_2$ ...(iii)

Adding Eqs. (i), (ii), and (iii), we get,

$K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + MnF_3 + \frac{1}{2}F_2$ ...(iv)

In Eq. (iii)

$e^- + \overset{+4}{Mn} \longrightarrow \overset{+3}{Mn}$ (n-factor = 1)

$F^{\ominus} \longrightarrow \frac{1}{2}F_2 + e^-$ (n-factor = 1)

Therefore, according to Eq. (iv)

$2\text{ mol of }SbF_5 \equiv 1\text{ mol of }K_2MnF_6$

$\equiv 1\text{ Eq of }K_2MnF_6$

∴ $1\text{ mol of }SbF_5 = \frac{1}{2}\text{ Eq} = 0.5\text{ Eq of }K_2MnF_6$

35. (4) $FeSO_4 + Fe_2(SO_4)_3 + KMnO_4 \xrightarrow{H^{\oplus}}$

Only $FeSO_4$ will be oxidised by $KMnO_4$.

mEq of $FeSO_4 \equiv$ mEq of $KMnO_4$

$= 2 \times 5 \times 100 = 1000$

mEq of $FeSO_4 = 1 =$ mol of $FeSO_4$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$$\Rightarrow x_{FeSO_4} = \frac{1}{3}$$

36. (4) $NO_3^{\ominus} + As_2S_3 \longrightarrow AsO_4^{3-} + NO + SO_4^{2-}$

$As_2S_3 + 20H_2O \longrightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 40H^{\oplus} + 28e^-$

$E_{As_2S_3} = \frac{M}{28}$ (n factor = 28) (electrons lost/mol)

37. (1) $M^{x+} + MnO_4^{\ominus} \longrightarrow MO_3^{\ominus} + Mn^{2+}$

$MnO_4^{\ominus} + 8H^{\oplus} + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$M^{x+} + 3H_2O \longrightarrow MO_3^{\ominus} + 6H^{\oplus} + (5 - x)e^-$

mEq of $MnO_4^{2-} \equiv$ mEq of M^{x+}

$1 \times 5 \equiv [1.67 \times (5 - x)] \Rightarrow 5 - x = 3 \Rightarrow x = 2$

38. (4) i. With phenolphthalein indicator: $NaHCO_3$ does not react with HCl whereas Na_2CO_3 reacts upto $NaHCO_3$ stage (50% reaction).

$V_{HCl} = x$ mL

ii. With methyl orange indicator: $NaHCO_3$ reacts completely with HCl and with Na_2CO_3 is 100% reaction. But y mL of HCl is added after Na_2CO_3 has reacted upto $NaHCO_3$. (i.e., half titre value of Na_2CO_3).

V_{HCl} = Full titre value of $NaHCO_3$ + Half titre value of Na_2CO_3.

y mL = Full titre value of $NaHCO_3$ + x mL

Full titre value of $NaHCO_3 = (y - x)$ mL

39. (1) In $NaHC_2O_4$, $C_2O_4^{2-}$ oxidised to CO_2 and $H^{\oplus}$ is neutralised.

$$Ew_{NaHC_2O_4} (\text{as } C_2O_4^{2-}) = \frac{M}{2}$$

$$(\text{as } H^{\oplus}) = \frac{M}{1}$$

$10 \times N_1 (NaHC_2O_4) = 10 \times 0.1\ N\ MnO_4^{\ominus}$

$N_1 = 0.1$ N

40. (1) $Fe_2(C_2O_4)_3 \equiv 3C_2O_4^{2-}$, Fe^{3+} is not affected

$2MnO_4^{\ominus} \equiv 5C_2O_4^{2-}$, $3C_2O_4^{2-} \equiv 1.2\ MnO_4^{\ominus}$

41. (1) 0.05 M Na_2CO_3 = 0.1 N Na_2CO_3

0.05 M $NaHCO_3$ = 0.05 N $NaHCO_3$

40 L of 0.1 Na_2CO_3 = 40 mL of 0.1 N HCl

(For complete reaction) = 80 mL of 0.05 M HCl

For 50% reaction = 40 mL of 0.05 M HCl

With phenolphthalein = x = 40 mL

40 mL of 0.05 $NaHCO_3$ = 40 mL of 0.05 M HCl

With methyl orange, $y = 80 + 40 = 120$ mL

$\therefore (y - x) = 80$ mL

42. (2) $\underset{0.05\text{ M}}{Cr_2O_7^{2-}} + \underset{0.6\text{ M}/200\text{ mL}}{FeC_2O_4} \xrightarrow{H^{\oplus}}$

$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \longrightarrow Fe^{3+} + e$;

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$

mEq of $K_2Cr_2O_7 \equiv FeC_2O_4$

$(0.05 \times 6) \times V = (0.6 \times 3) \times 200$

$\Rightarrow V = 1200$ mL = 1.2 L

43. (1) Remember it as a fact: in neutral medium, K_2MnO_4 (potassium manganate) disproportionate as follows:

$K_2MnO_4 \longrightarrow KMnO_4 + MnO_2$

On balancing, we get

$3MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^{\ominus} + 4\overset{\ominus}{O}H + MnO_2$

$1 \text{ mol } MnO_4^{2-} \equiv \frac{2}{3} \text{ mol } MnO_4^{\ominus} \equiv \frac{1}{3} \text{ mol } MnO_2$

44. (1) $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$

$MnO_4^{\ominus} + 8H^{\oplus} + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

Using mole concept

1 mol $MnO_4^{\ominus} \equiv$ 5 mol Fe^{2+}

and 1 mol $Cr_2O_7^{2-} \equiv$ 6 mol Fe^{2+}

So, $K_2Cr_2O_7$ will oxidise more Fe^{2+} to Fe^{3+}

45. (2) $\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\text{ L (at STP)}}{O_2}$

Mass of H_2O_2 in 1.5 N solution = Ew of $H_2O_2 \times 1.5$ N

$= 17 \times 1.5 = 25.5$ g

So, volume strength of 1.5 N H_2O_2 solution

$$= \frac{22.4 \text{ L} \times 25.5 \text{ g}}{68.0} = 8.4 \text{ L}$$

46. (2) $MnSO_4$

$x + 6 - 8 = 0, \quad x = 2$

In (1) Mn_2O_3, $\quad 2x - 6 = 0, x = 3$

In (2) MnO_2, $\quad x - 4 = 0, x = 4$

In (3) $MnO_4^{\ominus}$, $\quad x - 8 = -1, x = 7$

In (4) MnO_4^{2-}, $\quad x - 8 = -2, x = 6$

In (2), the change in oxidation number is $4 - 2 = 2$

Therefore, the answer is (2).

47. (2) Ew of $Na_2S_2O_3 = \frac{158}{n}$ $(n = 1)$

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \left(n = \frac{2}{2} = 1\right)$$

$MnO_4^{\ominus} = S_2O_3^{2-}$

mEq = mEq

$0.2M \times 5\ (n\text{-factor}) \times V = \frac{1.58}{158} \times 10^3$

$V = 10$ mL

48. (3) $S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 8e^-$

$3e^- + CrO_4^{2-} \longrightarrow [Cr(OH)_4]^{\ominus}$

$CrO_4^{2-} \equiv S_2O_3^{2-}$

mEq = mEq

$V \times 0.1 \times 3 \equiv 40 \text{ mL} \times 0.25 \times 8$

$V = 266.67$ mL

49. (2) $As_2O_3 \longrightarrow 2AsO_4^{3-} + 4e^-$

$5e^- + MnO_4^{\ominus} \longrightarrow Mn^{2+}$

$$\left(Ew \text{ of } As_2O_3 = \frac{2 \times 75 + 3 \times 16}{4} = \frac{198}{4}\right)$$

$As_2O_3 \equiv MnO_4^{\ominus}$

mEq ≡ mEq

$$\left(\frac{0.46}{198/4}\right) \times 10^3 \equiv 25 \times N$$

$N = 0.037$

$$M_{KMnO_4} = \frac{N}{5} = \frac{0.037}{5} = 0.074$$

50. (1) $Cr_2O_7^{2-} = Sn^{2+}$ $(Sn^{2+} \longrightarrow Sn^{4+} + 2e^-)$

$(n = 6)$ $(n = 2)$

1 Eq = 1 Eq

$$\frac{1}{6} \text{ mol} = \frac{1}{2} \text{ mol}$$

$$\therefore 1 \text{ mol of } Sn^{2+} = \frac{2}{6} \text{ mol of } Cr_2O_7^{2-}$$

$$= \frac{1}{3} \text{ mol of } Cr_2O_7^{2-}$$

51. (4) mEq of $H_2O_2 \equiv$ mEq $MnO_4^{\ominus}$

$$10 \text{ mL} \times N = 10 \text{ mL} \times \frac{1}{0.56}$$

$$N_{H_2O_2} = \frac{1}{0.56}$$

$1\ N_{H_2O_2} \equiv 5.6$ 'V'(volume strength of H_2O_2)

$$\frac{N}{0.56} H_2O_2 = 5.6 \times \frac{1}{0.56} = 10 \text{ 'V'}$$

52. (4) Refer to Concept Application Exercise 3.2 Q. 3(a).

53. (4) $CuCO_3 \Rightarrow \dfrac{3.1}{123.5/2} \times 1000$

$\equiv$ mEq $CuCO_3 \equiv$ mEq $H_3PO_4 = (0.5 \times 3) \times V$

$\Rightarrow V_{mL} = 33.3$ mL

54. (4) mEq Acid = mEq Base

$$\Rightarrow \frac{0.4}{Mw/n} \times 1000 = \frac{0.5}{40/1} \times 1000$$

$\Rightarrow n = 3$ and $H_nA \equiv 96 \Rightarrow A = 96 - 3 \times 1 = 93$

55. (1) KOH + Na_2CO_3

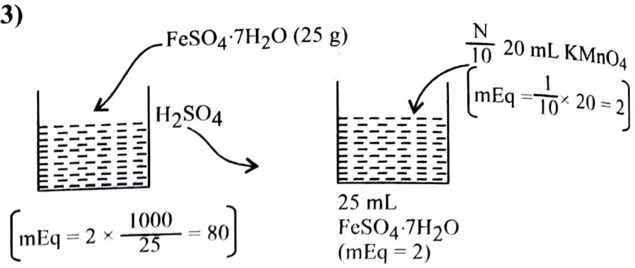
(x mmol) (y mmol)

i. $(x \times 1) + (y \times 2) \times \dfrac{1}{2} = \dfrac{1}{20} \times 15$

ii. $(x \times 1) + (y \times 2) = \dfrac{1}{20} \times 25 \Rightarrow y = 0.5$ and $x = 0.25$

$\Rightarrow$ KOH $\equiv x$ mmoles $= 0.25 \times 10^{-3} \times 56$ g $= 0.014$ g

56. (3)



$\Rightarrow$ mmol = 2

$[\because Fe^{2+} \longrightarrow Fe^{3+} + e^-]$

$$\Rightarrow \frac{(W_{FeSO_4 \cdot 7H_2O}) \times 1000}{278/1} = 80$$

$$\Rightarrow W_{FeSO_4 \cdot 7H_2O} = 22.24$$

$$\Rightarrow \% \text{ of } FeSO_4 \cdot 7H_2O = \frac{22.24}{25} \times 100\% = 88.96\%$$

57. (1) $MnO_2 + I^{\ominus} \longrightarrow I_2 + Mn^{2+}$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

[mEq $Na_2SO_3 = (1 \times 0.075) \times 30$]

mEq $Na_2S_2O_3$ = mEq I_2 = mEq MnO_2

$$\Rightarrow \frac{W_{MnO_2}}{87/2} \times 1000 = (1 \times 0.075) \times 30$$

$\Rightarrow$ % $MnO_2 = 75.3\%$

58. (1) $H_2C_2O_4 \longrightarrow 2CO_2 + 2H^{\oplus} + 2e^-$

$$\text{Moles } CO_2 = \frac{PV}{RT} = \frac{0.82 \times 5}{0.082 \times 350} = \frac{1}{7}$$

$$\Rightarrow mEq_{CO_2} = \frac{1}{7} \times 1\ mEq_{K_2Cr_2O_7}$$

$$\Rightarrow \frac{1}{7} = \frac{W_{K_2Cr_2O_7}}{294/6} \Rightarrow W_{K_2Cr_2O_7} = 7 \text{ g}$$

and $\dfrac{1}{7}$ mol $CO_2 \equiv \dfrac{1}{7}$ mol $H_2CO_3 \equiv 1 \times 2$ g Eq (acidic)

$= 0.1 \times V$

$= 2.86$ L

$V_{NaOH} = 2.86$ L

59. (2) $Na_2C_2O_4$; $KHC_2O_4 \cdot H_2C_2O_4$

x mmol y mmol

i. $x \times 0 + y \times 3 = 0.2 \times V$

ii. $x \times 2 + y \times 4 = (0.2 \times 5) \times V \Rightarrow \dfrac{x}{y} = \dfrac{11}{2}$

60. (2) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

Moles: 0.08 $4 \times 0.8 = 0.32$ $\dfrac{1.78}{22.4} = 0.08$

$\Rightarrow W_{MnO_2} = 0.08 \times 87$ g $= 6.96$ g;

$$\left(\frac{10 \times 4 \times 1.2}{36.5}\right) \times V_L = 0.32 \Rightarrow V_L = 0.24 \text{ L}$$

61. (4) Balance the reaction:

$$2CrO_5 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 2H_2O + \frac{7}{2}O_2$$

$\Rightarrow$ 1 mol CrO_5 liberates $\dfrac{7}{2}$ mol O_2

62. **(2)** mEq of $MnO_4^{\ominus} \equiv$ mEq of H_2O_2

$$10 \times \frac{M}{5} \times 5 \equiv \text{mEq of } H_2O_2$$

$$\Rightarrow 10 \text{ mEq} \equiv \text{mEq of } H_2O_2$$

$$\text{Weight of } H_2O_2 = 10 \times 10^{-3} \times \frac{34}{2} = 0.17 \text{ g}$$

$$\text{Weight of impure } H_2O_2 = \frac{100}{85} \times 0.17 = 0.2 \text{ g}$$

63. **(4)** Let x and y are the mEq of NaOH and Na_2CO_3, respectively.

Phenolphthalein as indicator:

$$\text{mEq of NaOH} = \frac{1}{2}\text{ mEq of } Na_2CO_3 = \text{mEq of HCl}$$

$$x + \frac{y}{2} = \frac{1}{2} \times 1 \times 20 = 10 \qquad \text{...(i)}$$

Methyl orange as indicator:

$$\frac{\text{mEq } Na_2CO_3\text{(left)}}{2} = \text{mEq of HCl}$$

$$\frac{y}{2} = \frac{1}{2} \times 8 = 4 \qquad \text{...(ii)}$$

$$y = 8,\ x = 6$$

$$\text{Weight of } Na_2CO_3 = 8 \times 10^{-3} \times \frac{106}{2} = 0.424 \text{ g}$$

$$\% \text{ of } Na_2CO_3 = \frac{0.424}{0.848} \times 100 = 5\%$$

Multiple Correct Answers Type

1. **(1, 4)**

Case I: $MnO_4^{\ominus} \equiv FeC_2O_4$
$(n = 5)$ $\quad (n = 3)$

$$\left[\begin{array}{l} \overset{+2}{Fe} \longrightarrow \overset{+3}{Fe} + e^- \\ C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \end{array}\right] n = 3$$

$$V \times 0.1 \times 5 \equiv 100 \times 0.1 \times 3$$

$$V = 60 \text{ mL}$$

Case II: $MnO_4^{\ominus} \equiv Fe_2(C_2O_4)_3$ $\quad$ [oxidation reducing agent]
$(n = 5)$ $\quad (n = 6)$

$$\left[\begin{array}{l} Fe^{3+} \text{ does not oxidise} \\ 3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^- \end{array}\right]$$

$$V \times 0.1 \times 5 \equiv 100 \times 0.1 \times 6$$

$$V = 120 \text{ mL}$$

2. **(2, 4)**

Since $Cr_2O_7^{2-}$ is reduced to Cr^{3+}, so H_2O_2 must be oxidised to O_2.

Oxidation number of Cr in $Cr_2O_7^{2-}$ is +6 and +3 in Cr^{3+}. So, change in oxidation number = 3. Hence statements (b) and (d) are wrong.

3. **(1, 2, 3)**

(1) $MnO_4^{\ominus} + 8H^{\oplus} + 5e^- \longrightarrow Mn^{2-} + 4H_2O$
(0.1 mol)

mEq of $MnO_4^{\ominus} = 0.1 \times 5 = 0.5$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$
(0.5 mol)

$\Rightarrow$ mEq of $Fe^{2+} = 0.5$

(2) $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$
(0.166 mol)

$\Rightarrow$ mEq of $FeC_2O_4 = 0.166 \times 3 = 0.5$

(3) $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$
(0.25 mol)

$\Rightarrow$ mEq of $C_2O_4^{2-} = 0.25 \times 2 = 0.5$

(4) $Cr_2O_7^{2-}$ being an oxidising agent cannot be oxidised.

4. **(2, 4)**

$H_2C_2O_4$: As acid, $n = 2$
As reducing agent, $n = 2$

$NaHC_2O_4$: As acid, $n = 1$
As reducing agent, $n = 2$

$$[E_{H_2C_2O_4}]_{\text{as reducing agent}} = \frac{M}{2}$$

$$[E_{NaHC_2O_4}]_{\text{as reducing agent}} = \frac{M}{2}$$

On reaction with $KMnO_4$

$H_2C_2O_4$ and $NaHC_2O_4$: both are acting as reducing agents with same n factor of 2.

mEq of $KMnO_4 \equiv$ mEq of $H_2C_2O_4$

mEq of $KMnO_4 \equiv$ mEq of $NaHC_2O_4$

5. **(1, 2)**

The possible formula be $A_xB_yC_z$.

As compound is neutral, so $x(+2) + y(+5) + z(-2) = 0$

$$\Rightarrow 2x + 5y - 2z = 0$$

By hit and trial, we get: $x = 1, y = 2, z = 6$ and $x = 3, y = 2, z = 8$

So compound is $A(BC_3)_2$ or $A_3(BC_4)_2$.

6. **(1, 2, 3, 4)**

(1) mEq of $Fe^{2+} = 1 \times 5 = 5$

mEq of $MnO_4^{\ominus} = 1 \times 5 = 5$

(2) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^{\oplus} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

1 mol $Cr_2O_7^{2-} \equiv$ 6 mol Fe^{2+}

(3) Find n factor of Cu_2S

$$\begin{array}{l} Cu_2^{2+} \longrightarrow 2Cu^{2+} + 2e^- \\ S^{2-} \longrightarrow \overset{+4}{S}O_2 + 6e^- \\ \hline 1 \text{ mol } Cu_2S \equiv 8 \text{ mol } e^- \\ \hline \end{array}$$

$\Rightarrow$ mEq of $Cu_2S = 1 \times 8 = 8$

Now mEq of $MnO_4^{\ominus}$ (acidic) $= 5 \times 1.6 = 8$

(4) $Cu^{2+} \longrightarrow Cu^{2+}$ (not a redox reaction)

$S^{2-} \longrightarrow SO_2 + 6e^-$

$\Rightarrow$ 1 mol CuS $\equiv$ 6 mol e^-

⇒ n-factor of Cus = 6

mEq of CuS = $1 \times 6 = 6$

mEq of $Cr_2O_7^{2-} = 1 \times 6 = 6$

7. (1, 2)

i. $5e^- + MnO_4^{\ominus} \longrightarrow Mn^{2+}$

ii. $Br_2 \longrightarrow 2BrO_3^{\ominus} + 10e^-$

iii. $2MnO_4^{\ominus} + Br_2 + 8H^{\oplus} \longrightarrow 2Mn^{2+} + 2BrO_3^{\ominus} + 2H_2O$

$$Ew(MnO_4^{\ominus}) = \frac{M_1}{5}\ (n = 5)$$

$$Ew(Br_2) = \frac{M_2}{10}\ (n = 6)$$

(3) n-factor ratio $(MnO_4^{\ominus}/Br_2) = \frac{5}{6}$

8. (1, 2, 3, 4)

(1) 1.7% = 1 N

6.8% = 4 N

(2) $M = \frac{4\text{ N}}{2} = 2\text{ M}$

(3) 1.7% = 5.6 'V'

6.8% = 22.4 'V'

(4) Volume strength = $5.6 \times N = 5.6 \times 2 \times M = 11.2 \times M$

9. (1, 2, 3)

I. In $\left(\overset{+5\times2}{As_2}\ \overset{-2\times5}{S_5}\right)$,

$$\left[\begin{array}{ccc} \overset{+5}{As_2} & \xrightarrow[\text{redox}]{\text{no}} & 2AsO_4^{3-} \\ 2x = 10 & & 2x - 16 = -6 \\ & & 2x = 10 \end{array}\right] \boxed{n = 0} \quad ...(i)$$

$$\begin{array}{ccccc} S_5^{-2} & \longrightarrow & 5SO_4^{2-} & + & 40e^-\,] \\ 5x = -10 & & 5x - 40 = -10 & & \\ & & 5x = 30 & & \end{array} \quad ...(ii)$$

Add Eqs. (i) and (ii), we get

$As_2S_5 \longrightarrow 2AsO_4^{3-} + 5SO_4^{2-} + 40e^- \qquad (n = 40)$

$$Ew = \frac{M}{40}$$

II. Reduction :

$$\left[\begin{array}{ccc} 3e^- + NO_3^{\ominus} & \longrightarrow & NO_2 \\ x - 6 = -1 & & x - 4 = 2 \\ x = 5 & & x = 2 \end{array}\right] n = 3$$

10. (2, 3, 4)

pOH = 1, strong basic medium

⇒ $MnO_4^{\ominus} \longrightarrow MnO_4^{2-}$ (n-factor = 1)

$2\overset{\ominus}{O}H + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$

mEq of H_2O_2 = mEq of $MnO_4^{\ominus}$

$$\frac{x}{34/2} \times 1000 = 1100 \times \left(\frac{1}{5} \times 1\right)$$

$x = 0.34$ g

11. (1, 3)

$Na_2C_2O_4$ and $NaHC_2O_4$ both reacts with H_2O_2 as reducing agent only. (n factor for both = 2)

With H_2O_2:

Eq of H_2O_2 = Eq of $Na_2C_2O_4$ + Eq of $NaHC_2O_4$

$2 \times$ moles of $H_2O_2 = n_1 \times 2 + n_2 \times 2$

$$\text{moles of } H_2O_2 = \frac{2\,(n_1 + n_2)}{2} = (n_1 + n_2)$$

With KOH: Only $NaHC_2O_4$ reacts with KOH as acid–base titration, n factor = 1 (one $H^{\oplus}$ ion)

Eq of KOH = Eq of $NaHCO_3$

$1 \times$ moles of KOH $= n_2 \times 1$

moles of KOH $= n_2$

∴ Moles of H_2O_2 and KOH are: $(n_1 + n_2)$ and n_2.

n-factor of $NaHC_2O_4$ with KOH and H_2O_2 = 1 and 2

n-factor of $Na_2C_2O_4$ with H_2O_2 and KOH = 2 and 2

12. (2, 3, 4)

(1) $5e^- + MnO_4^{\ominus} \longrightarrow Mn^{2+}\ (n = 5)$

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \left(n = \frac{2}{2} = 1\right)$

Eq of $MnO_4^{\ominus}$ ≡ Eq of $S_2O_3^{2-}$

$5 \times$ moles of $MnO_4^{\ominus} \equiv 1 \times$ moles of $S_2O_3^{2-}$

∴ 1 mol of $S_2O_3^{2-}$ = 5 mol of $MnO_4^{\ominus}$

(2) pH changes from 4 to 10 (acidic to strongly basic)

$e^- + MnO_4^{\ominus} \longrightarrow MnO_4^{2-}\ (n = 1)$

$S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 8e^-\ (n = 8)$

Eq of $MnO_4^{\ominus}$ = Eq of $S_2O_3^{2-}$

$1 \times$ moles of $MnO_4^{\ominus} \equiv 8 \times$ moles of $S_2O_3^{2-}$

∴ 1 mol of $S_2O_3^{2-} = \frac{1}{8}$ mol of $MnO_4^{\ominus}$

Hence with change of pH from 4 to 10, will change the stoichiometry of reaction and also changes the product.

(3) pH changes from 4 to 7 (acidic to neutral medium)

$3e^- + MnO_4^{\ominus} \longrightarrow MnO_2\ (n = 3)$

$S_2O_3^{2-} \longrightarrow 2HSO_4^{\ominus} + 8e^-\ (n = 8)$

Hence it will also effect the stoichiometry of reaction and nature of product.

(4) At pH = 7, $S_2O_3^{2-}$ is oxidised to $HSO_4^{\ominus}$ ion.

13. (1, 2, 4)

i. mEq H_2O_2 ≡ mEq of $Cr_2O_7^{2-}$

$(n = 2)\quad (n = 6)$

$20\text{ mL} \times N_1 = 40\text{ mL} \times N_2$ ...(i)

(1) mEq of $Cr_2O_7^{2-}$ ≡ mEq of $C_2O_4^{2-}$

$(n = 2)$

$2.0 \times N_2 \equiv 5.0 \times 1.0 \times 2$

$N_2(Cr_2O_7^{2-}) = 5$ ...(ii)

Therefore, substituting the N_2 in Eq. (i)

$20\text{ mL} \times N_1 = 40\text{ mL} \times 5$

$N_1(H_2O_2) = 10$

$$M_1(H_2O_2) = \frac{10}{2} = 5\,M$$

(2) 1 N H_2O_2 = 5.6 V

∴ 10 N H_2O_2 = 56 V

(4) $N_1V_1 + N_2V_2 = N_3V_3$ ($V_3 = 10 + 40 = 50$ mL)

$$10 \times 10 + 40 \times \frac{5}{8} \times 2 = N_3 \times 50$$

N_3 (final) $H_2O_2 = 3$ N

The volume strength of $H_2O_2 = 5.6 \times 3 = 16.8$ V

14. **(1, 2, 4)**

All three are self indicators i.e., they do not need any indicator for titration.

$$K_2S_2O_3 = \frac{0.19}{190} = 10^{-3} \text{ mol} = 1 \text{ mmol}$$

i. mEq of $S_2O_3^{2-}$ ($n = 8$) = mEq of $Cr_2O_7^{2-}$ ($n = 6$)

$1 \times 8 = 0.1 \times 6 \times V$

$$\therefore V_{Cr_2O_7^{2-}} = \frac{80}{6} \text{ mL}$$

ii. mEq of $S_2O_3^{2-}$ ($n = 1$) = mEq of I_2 ($n = 2$)

$1 \times 1 = 0.1 \times 2 \times V$

$\therefore \quad V_{I_2} = 5$ mL

iii. mEq of $S_2O_3^{2-}$ ($n = 8$) = mEq of $MnO_4^{\ominus}$ ($n = 3$)

$1 \times 8 = 0.1 \times 3 \times V$

$$\therefore V_{MnO_4^{\ominus}} = \frac{80}{3} \text{ mL}$$

Also,

$$\text{Weight of } K_2Cr_2O_7 = 8 \times \frac{294}{6} \times 10^{-3} = 0.392 \text{ g}$$

$$\text{Weight of } I_2 = 1 \times \frac{254}{2} \times 10^{-3} = 0.127 \text{ g}$$

$$\text{Weight of } KMnO_4 = 8 \times \frac{158}{3} \times 10^{-3} = 1.264 \text{ g}$$

15. **(2, 4)**

Since 2 mol of $HCO_3^{\ominus}$ is present. So there should be one mole each of $CaCO_3$, $CaCl_2$ and $MgCl_2$ to have equal hardness.

$\therefore$ *Mw* of $HCO_3^{\ominus} = 61$,

ppm of $HCO_3^{\ominus} = 61 \times 2 = 122$ g in 10^6 mL H_2O

[*Mw* of $CaCO_3 = 100$, *Mw* of $CaCl_2 = 111$, *Mw* of $MgCl_2 = 95$ g mol^{-1}]

1 mol of $CaCO_3 \equiv 100$ ppm

1 mol of $CaCl_2 = 111$ ppm

1 mol of $MgCl_2 = 95$ ppm

Hence, answer is (2) and (4).

Linked Comprehension Type

1. **(2)** $MnO_4^{\ominus} \equiv S_2O_3^{2-} \quad (2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-)$

(acidic)

'n' factor = 5 'n' factor = 1 $\left(n = \frac{2}{2} = 1\right)$

100 mL × $N \equiv$ 100 mL × 0.1 × 1 (n factor)

$N = 0.1$

$$M = \frac{0.1}{n \text{ factor}} = \frac{0.1}{5} = 0.02 \text{ M}$$

2. **(1)** $MnO_4^{\ominus} \equiv S_2O_3^{2-}$ ($S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 8e^-$) ($n = 8$)

(basic)

n factor = 1 n factor = 8

100 mL × $N \equiv$ 100 mL × 0.1 × 8

$N = 0.8$

$$M = \frac{N}{n \text{ factor}} = 0.8 \text{ M}$$

3. **(3)** $MnO_4^{\ominus} \equiv S_2O_3^{2-}$ ($S_2O_3^{2-} \longrightarrow 2HSO_4^{\ominus} + 8e^-$) ($n = 8$)

(aqueous)

n factor = 3 n factor = 8

100 mL × $N \equiv$ 100 mL × 0.1 × 8

$N = 0.8$

$$M = \frac{0.8}{3} = 0.26$$

4. **(4)** $d_{sol} = M\left(\frac{Mw_2}{1000} + \frac{1}{m}\right)$

$M = 0.02$ (from Q. 1)

$$1.58 = 0.02\left(\frac{158}{1000} + \frac{1}{m}\right)$$

Solve for m :

$m = 0.012$

5. **(2)** Refer to Illustration 3.50

6. **(1)** Total mmoles $BrO_3^{\ominus} = 20 \times \frac{1}{60} = \frac{1}{3}$

$$\text{Total mmoles of } AsO_2^{\ominus} = \frac{1}{60} \times 5 = \frac{1}{12}$$

According to the balanced equation for first and second reaction

$5SeO_3^{2-} + 2BrO_3^{\ominus} + 2H^{\oplus} \longrightarrow 5SeO_4^{2-} + Br_2 + H_2O$

5 mmol 2 mmol ...(i)

$BrO_3^{\ominus} + 3AsO_2^{\ominus} + H_2O \longrightarrow Br^{\ominus} + 3AsO_4^{3-} + 6H^{\oplus}$

1 mmol 3 mmol ...(ii)

$\because$ 3 mmol of $AsO_2^{\ominus}$ = 1 mmol of $BrO_3^{\ominus}$ in Eq. (ii)

$$\frac{1}{12} \text{ mmol of } AsO_2^{\ominus} = \frac{1}{3} \times \frac{1}{12}$$

$$= \frac{1}{36} \text{ mmol of excess } BrO_3^{\ominus}$$

mmoles of $BrO_3^{\ominus}$ reacted with SeO_3^{2-} in Eq. (i)

$$= \frac{1}{3} - \frac{1}{36} = \frac{11}{36} \text{ mmol of } BrO_3^{\ominus} \text{ reacted}$$

[$BrO_3^{\ominus} \equiv AsO_2^{\ominus}$] Eq. (ii)

mEq ≡ mEq

$$\frac{1}{36} \text{ mmol} = \frac{1}{12} \text{ m mol}$$

$$\frac{1}{36} \times 6 \text{ mEq} = \frac{1}{12} \times 2 \text{ mEq}$$

$$\frac{1}{6} \text{ mEq excess mEq of } BrO_3^{\ominus} \equiv \frac{1}{6} \text{ mEq}$$

Hence, answer is (1) = $\frac{1}{6}$ mEq

7. (2) mmoles of $BrO_3^{\ominus}$ reacted with SeO_3^{2-} in Eq. (i)

$= \frac{11}{36}$ mmol of $BrO_3^{\ominus}$

$= \frac{11}{36} \times 5$ (*n*-factor $BrO_3^{\ominus}$ in Eq. (i))

$= \frac{55}{36}$ mEq of $BrO_3^{\ominus} \equiv$ mEq of SeO_3^{2-} reacted

8. (4) mEq of $SeO_3^{2-} = \frac{55}{36}$

Weight of SeO_3^{2-} = mEq $\times 10^{-3} \times Ew$

(Ew of $SeO_3^{2-} = \frac{127}{2}$) ($n = 2$)

$= \frac{55}{36} \times 10^{-3} \times \frac{127}{2}$ g

$= 0.097$ g $= 97$ mg

9. (1) (T), (2) (F), (3) (T), (4) (F)

10. (2) $\left. 10e^- + \underset{\substack{2x-16=-2\\2x=14}}{2MnO_4^{\ominus}} \longrightarrow \underset{2x=4}{2\overset{+2}{Mn}} \right] n = 10$

FeC_2O_4 ($n = 3$),

($Fe^{2+} \longrightarrow Fe^{3+} + e^-$, and $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$)

$FeC_2O_4 \equiv Ba^{2+} (MnO_4^{-1})_2 \equiv CO_2$

$C_2O_4^{2-} \equiv (MnO_4^{-1})_2 \equiv CO_2 \equiv 20 \times \frac{1}{10} \times 10$

mEq mEq mEq

20 mEq ≡ 20 mEq ≡ 20 mEq

11. (1) $\frac{20}{3}$ mmol of FeC_2O_4

$\frac{20}{10} = 2$ mmol of $Ba(MnO_4)_2$

12. (2) 1 eq of $CO_2 = \frac{22.4}{2}$ L $= 11.2$ L at STP

1000 mEq of $CO_2 = 11200$ mL at STP

20 mEq of $CO_2 = \frac{11200}{1000} \times 20 = 224$ mL

13. (1) $2Cu^{2+} + 2e^- \longrightarrow Cu_2^{\oplus}$

Number of e^-'s transfer per mol $= \frac{2}{2} = 1$

Ew of $CuSO_4 = \frac{Mw}{n\text{-factor}} = \frac{Mw}{1}$

14. (2) $CuSO_4 + KI \longrightarrow I_2 \longrightarrow S_2O_3^{2-}$

(638 g) 0.2M 400 mL of 1.0 M

$2Cu^{2+} + 2e^- \longrightarrow Cu_2^{\oplus}$

$2I^{\ominus} \longrightarrow I_2 + 2e^-$

$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^{\ominus} + S_4O_6^{2-}$

2 mol $CuSO_4 \equiv$ 4 mol KI ≡ 1 mol I_2

≡ 2 mol $S_2O_3^{2-}$

m mol $CuSO_4 \equiv$ mmol $S_2O_3^{2-}$

≡ 400 × 1 mmoles = 0.4 mol

Weight of $CuSO_4 \equiv 400 \times 10^{-3} \times 159.5$ g

% $CuSO_4 = \frac{400 \times 10^{-3} \times 159.5 \times 100}{638} = 10\%$

15. (3) 1 mol $CuSO_4 \equiv$ 1 mol $S_2O_3^{2-}$

$\equiv \frac{1}{2}$ mol $I_2 \equiv$ 2 mol. KI

$\equiv 0.4 \times 2 = 0.8$ mol

$\therefore 0.2\, M \times V = 0.8$

$V = 4$ L

16. (3) $NaHCO_3 \xrightarrow{\text{Phenolphthalein}}$ No reaction

So, mEq of HCl = mEq KOH

50 × 0.2/100 mL

= 50 × 0.2 × 10/1000 mL

= 100 mEq

$= 100 \times 10^{-3} \times 56$ g of KOH

= 5.6 g

Weight of $NaHCO_3 = (10 - 5.6) = 4.4$ g

% of $NaHCO_3 = \frac{4.4}{10} \times 100 = 44\%$

17. (3) Let *a* and *b* mEq of Na_2CO_3 and NaOH are present in the mixture.

When phenolphthalein is used as indicator

$\frac{a}{2}$ mEq of Na_2CO_3 + *b* mEq of NaOH = mEq of HCl

$\frac{a}{2} + b = 20 \times 0.4 \times 1 = 8$ ...(i)

When methyl orange is used as indicator

a mEq of Na_2CO_3 + *b* mEq of NaOH = mEq of HCl

$a + b = 25 \times 0.4 \times 1 = 10$ ...(ii)

Solve for *a* and *b* from Eqs. (i) and (ii)

$a = 4$ mEq $= \frac{4}{2}$ mmol = 2mmol

$b = 6$ mEq $= \frac{6}{1}$ mmol = 6 mmol

Ratio of Na_2CO_3:NaOH = 2:6 = 1:3

18. (2) From Q. 17. mEq of NaOH = 6 mEq $(100\text{ mL})^{-1}$

= 60 mEq $(1000\text{ mL})^{-1}$

$= 60 \times 10^{-3} \times 40$ g L^{-1}

= 2.4 g L^{-1}

19. (1) From Q. 17, mmol of Na_2CO_3 = 2 mmol $(100\text{ mL})^{-1}$

= 20 mmol $(1000\text{ mL})^{-1}$

$= 20 \times 10^{-3} \times 106$ g $L^{-1} = 2.12$ g L^{-1}

20. (4) The problem can be solved simply by mol concept since *n* factor for both H_2O_2 and Sn^{2+} is 2.

$2H^{\oplus} + \underset{1\text{ mol}}{H_2O_2} + \underset{1\text{ mol}}{Sn^{2+}} \longrightarrow Sn^{4+} + 2H_2O$

mmol of H_2O_2 = mmol of Sn^{2+}

= 100 mL × 3 M = 300 mmol

= 300 mmol of H_2O_2

= 300 × 2(*n* factor) mEq H_2O_2

= 600 mEq = 0.6 eq

21. (2) Mol of H_2O_2 initially present $= 136\text{ g} \times \frac{10}{100} \times \frac{1}{34}$

$= 0.4$ mol of H_2O_2

Mol of H_2O_2 left = (Mol of H_2O_2 initially present − Mol of H_2O_2 reduced by Sn^{2+})

$= 0.4 - 0.3 = 0.1$ mol of H_2O_2 left

Equivalent of H_2O_2 left $= 0.1 \times 2 = 0.2$ eq/100 mL

22. (2) 1 N or Eq L^{-1} of $H_2O_2 = 5.6$ volume of O_2 at STP

(Volume of strength of H_2O_2)

$$\Rightarrow N = \frac{0.2}{100} \times 1000 = 2 \text{ Eq } L^{-1} \text{ of } H_2O_2$$

$$= 5.6 \times 2 = 11.2 \text{ V}$$

23. (1) $2H_2O_2 \longrightarrow 2H_2O + O_2$

2 mol 1 mol

2 mol of H_2O_2 gives 1 mol of O_2

0.1 mol of H_2O_2 gives 0.1 mol of O_2

$$V = \frac{nRT}{P} = \frac{0.1 \times 0.082 \times 300}{1} = 2.46 \text{ L}$$

24. (2) $As_2S_3 + NaOH + H_2O_2 \longrightarrow AsO_4^{3-} + H_2O + SO_4^{2-}$

Oxidation:

$$As_2^{3+} + 16\overset{\ominus}{O}H \longrightarrow 2AsO_4^{3-} + 8H_2O + 4e^- \quad \text{...(i)}$$

$$S_3^{2-} + 24\overset{\ominus}{O}H \longrightarrow 3SO_4^{2-} + 12H_2O + 24e^- \quad \text{...(ii)}$$

$$As_2S_3 + 40\overset{\ominus}{O}H \longrightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O + 28e^- \quad \text{...(iii)}$$

Reduction:

$$H_2O_2 + 2e^- \longrightarrow 2\overset{\ominus}{O}H \quad \text{...(iv)}$$

Multiply Eq. (iv) by 14 and add Eqs. (iii) and (iv) to get

$$As_2S_3 + 12\overset{\ominus}{O}H + 14H_2O_2 \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O$$

Ans. 1 12 14 2 3 20 ...(v)

25. (1) Initial mmoles of $As_2S_3 = 0.4 \times 100 = 40$

Initial mmoles of NaOH $= 5 \times 100 = 500$

Initial mmoles of $H_2O_2 = 6 \times 100 = 600$

Balanced Eq. (v) shows that As_2S_3 is the limiting reagent

$$As_2S_3 + 12OH + 14H_2O_2 \longrightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O$$

(Initial mmoles) ⇒	40	500	600	—	—	—
(mmoles of reactant and mmoles of product formed) ⇒	40	$12 \times 40 = 480$	$14 \times 40 = 560$	$2 \times 40 = 80$	$3 \times 40 = 120$	$20 \times 40 = 800$
(m moles of reactant left) ⇒	$40-40 = 0$	$500 - 480 = 20$	$600 - 560 = 40$	80	120	800
(M of species left total volume = 300 mL) ⇒	0	$\left(\frac{20}{300}\text{M} = \frac{\text{M}}{15}\right)$	$\left(\frac{40}{300}\text{M} = \frac{2\text{M}}{15}\right)$	$\left(\frac{80}{300}\text{M} = \frac{4\text{M}}{15}\right)$	$\left(\frac{120}{300}\text{M} = \frac{6\text{M}}{15}\right)$	$\left(\frac{800}{300}\text{M} = \frac{8\text{M}}{3}\right)$

26. (3) If a H_2O_2 solution is allowed to stand, it decomposes to O_2 and H_2O

$$\underset{40}{H_2O_2} \longrightarrow \underset{0}{H_2O} + \underset{0}{\frac{1}{2}O_2}$$

mmoles of H_2O_2 left — $\frac{1}{2} \times 40 = 20$ mmol of O_2

Thus, mmoles of O_2 formed $= 40 \times \frac{1}{2} = 20$

Volume of O_2 at STP $= 20 \times 10^{-3} \times 22.4$ L

($\because$ 1 mol of O_2 at STP = 22.4 L)

$= 0.448$ L

27. (3) M of H_2O_2 left $= \frac{2\text{M}}{15}$

N of H_2O_2 left $= \frac{2 \times 2}{15} = \frac{4}{15}$ N

1 N of $H_2O_2 = 1$ eq/L $H_2O_2 = 5.6$ 'V'

(Volume strength) = 1.7%

$$\frac{4}{15}\text{ N } H_2O_2 = 1.7 \times \frac{4}{15} = 0.452\%$$

28. (1) $Fe + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4$

1 mol ≡ 3 mol

1 mol of $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O \equiv 1$ mol $Fe_2(SO_4)_3$

$\frac{2.41}{964}$ mol of ferric alum $\equiv \frac{2.41}{964}$ mol of $Fe_2(SO_4)_3$.

$\equiv \frac{3 \times 2.41}{964}$

$= 0.0075$ mol of $FeSO_4$

29. (2) If Cu were used in place of Fe

$Cu + Fe_2(SO_4)_3 \longrightarrow 2FeSO_4 + CuSO_4$

1 mol 2 mol

Note: Only $FeSO_4$ reacts with $K_2Cr_2O_7$ not $CuSO_4$. Since ($Fe^{2+} \longrightarrow Fe^{3+} + e^-$) but Cu^{2+} does not change.

$\frac{2.41}{964}$ mol of $Fe_2(SO_4)_3 \equiv 2 \times \frac{2.41}{964}$ mol of $FeSO_4$

$\equiv 0.005$ mol of $FeSO_4$

30. (3) mEq of $FeSO_4 \equiv$ mEq of $K_2Cr_2O_7$

$$\left(\frac{3 \times 2.41}{964}\right) \times 10^3 \equiv \frac{1}{60} \times 6\ (n\text{ factor}) \times V\text{ (mL)}$$

$V = 75$ mL

$(Fe^{2+} \longrightarrow Fe^{3+} + e^-)\ (6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+})$

31. (2) mEq of $FeSO_4 \equiv$ mEq of $K_2Cr_2O_7$

$$\left(\frac{2 \times 2.41}{964}\right) \times 10^3 \equiv \frac{1}{60} \times 6 \times V$$

$V = 50$ mL

32. (1) In first titration, both H_2SO_4 and $H_2C_2O_4$ react with base, as acid–base titration. n factor for both is 2 due to $2H^{\oplus}$ per mol in each case. Let x = mEq of $H_2C_2O_4$ and y = mEq of H_2SO_4.

$\therefore$ mEq of $H_2C_2O_4$ + mEq of H_2SO_4 = mEq of KOH

$\therefore x + y = 20 \times 0.1 \times 1$ (n-factor)

$x + y = 2$ ...(i)

In second titration, only $H_2C_2O_4$ (being reducing agent) reacts with $K_2Cr_2O_7$.

$$\therefore \underset{(n=2)}{\text{mEq of } H_2C_2O_4} \equiv \underset{(n=6)}{\text{mEq of } K_2Cr_2O_7}$$

$$(C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-) \quad (6e^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+})$$

$$(x) = \text{mEq of } H_2C_2O_4 \equiv 50 \times \frac{1}{300} \times 6$$

$\therefore x \equiv 1$ mEq ...(ii)

From Eqs. (i) and (ii), we get

$x = 1$ mEq, $y = 1$ mEq

Weight of $H_2C_2O_4 = 1 \times 10^{-3} \times 45$

$$\left(Ew \text{ of } H_2C_2O_4 = \frac{90}{2} = 45\right)$$

$$= 0.045 \text{ g/10 mL}$$

$$= \frac{0.045 \times 1000}{10} \text{ g L}^{-1} = 4.5 \text{ g L}^{-1}$$

Therefore, strength of $H_2C_2O_4 = 4.5$ g L^{-1}

> **Note:** In the above reaction, H_2SO_4 also reacts with $K_2Cr_2O_7$, but in the same reaction with $H_2C_2O_4$, the mEq of H_2SO_4 should not be added separately.
>
> $$H_2C_2O_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow 2Cr^{3+} + CO_2$$

33. (2) mEq of $H_2SO_4(y) = 1$

Weight of $H_2SO_4 = 1 \times 10^{-3} \times 49$

$$\left(Ew \text{ of } H_2SO_4 = \frac{98}{2} = 49\right)$$

$$= 0.049 \text{ g/10 mL}$$

$$= \frac{0.049 \times 1000}{10} \text{ g L}^{-1}$$

Therefore, the strength of $H_2SO_4 = 4.9$ g L^{-1}

34. (2) mEq of H_2O_2 = mEq of $K_2Cr_2O_7$

$$= 1 \text{ mEq/10 mL}$$

$$= \frac{1 \times 10^{-3} \times 10^3}{10} \text{ Eq L}^{-1} = 0.1 \text{ N}$$

Volume strength of $H_2O_2 = 0.1 \times 5.6 = 0.56$ '*V*'

Matrix Match Type

1. (a → q) $MnO_4^{\ominus} = Fe^{2+}$

$$(n=5) \quad (n=1)$$
$$1 \text{ Eq} = 1 \text{ Eq}$$
$$\frac{1}{5}\text{mol} = \frac{1}{1}\text{mol}$$
$$1 \text{ mol} = 5 \text{ mol}$$

(b → r) $CuS \equiv Cr_2O_7^{2-}$

$$(n=6) \quad (n=6)$$
$$1 \text{ Eq} = 1 \text{ Eq}$$
$$1 \text{ mol} = 1 \text{ mol}$$

(c → s) $Cu_2S = MnO_4^{\ominus}$

$$(n=8) \quad (n=5)$$
$$1 \text{ Eq} = 1 \text{ Eq}$$
$$\frac{1}{8}\text{mol} = \frac{1}{5}\text{mol}$$
$$1 \text{ mol} = \frac{8}{5} = 1.6$$

(d → p) $Cr_2O_7^{2-} = Fe^{2+}$

$$(n=6) \quad (n=1)$$
$$1 \text{ Eq} = 1 \text{ Eq}$$
$$\frac{1}{6}\text{mol} = \frac{1}{1}\text{mol}$$
$$1 \text{ mol} = 6 \text{ mol}$$

2. (a → s) Mixture A: $(NaOH + Na_2CO_3)$

$$\underbrace{p_{\text{mEq}} \qquad q_{\text{mEq}}}_{100 \text{ mL}}$$

With phenolphthalein: (NaOH reacts completely and 1/2 mEq of Na_2CO_3 reacts)

$$p + \frac{q}{2} - = a \times 1 \quad \text{...(i)}$$

with methyl orange (both react completely):

$$p + q = b \times 1 \quad \text{...(ii)}$$

Solve: $\frac{q}{2} = (b - a)$, $q = 2(b - a)$

mmoles of Na_2CO_3 $(q) = 2(b - a)$

mmoles of Na_2CO_3 $(q) = \frac{2(b-a)}{2} = (b - a)$ mmol

(b → r) Mixture B: $(NaHCO_3 + Na_2CO_3)$

$$\underbrace{r_{\text{mEq}} \qquad s_{\text{mEq}}}_{100 \text{ mL}}$$

With phenolphthalein: ($NaHCO_3$ does not react) Na_2CO_3 react half)

$$\therefore \frac{s}{2} = x \times 1 \text{ mEq of } Na_2CO_3$$

$$s = 2x \text{ mEq of } Na_2CO_3 = \frac{2x}{2}$$

$$= x \text{ mmol of } Na_2CO_3$$

With methyl orange (both reacts completely):

$$r + s = y \times 1 \text{ mEq}$$
$$r + 2x = y$$

(d → q) $r = (y - 2x)$ mEq = mmoles of $NaHCO_3$

(c → p) NaOH in mixture A:

Solve Eqs. (i) and (ii)

$$2p + \frac{3}{2}q = a + b$$

Substitute the value of $q = 2(b - a)$

$$2p + \frac{3}{\cancel{2}} \times \cancel{2}(b - a) = a + b$$

$$2p = a + b - 3b + 3a = 4a - 2b$$

$p = (2a - b)$ mEq = mmoles of NaOH

3. (a → q)

$$\underset{2x=0}{Br_2} \longrightarrow \underset{\substack{2x-12=-2 \\ 2x=10}}{2BrO_3^{\ominus}} + 10e^- \; (n = 10) \qquad Ew \text{ of } Br_2 = \frac{M}{10}$$

(b → p)

$$Br_2 \longrightarrow 2BrO_3^{\ominus}\ (n = 10)$$

$$2e^- + Br_2 \longrightarrow 2Br^{\ominus}\ (n = 2)$$

$$Ew \text{ of } Br_2 = \frac{M}{10} + \frac{M}{2} = \frac{6M}{10} + \frac{3M}{5}$$

(c → s)

$$H_2C_2O_4 \longrightarrow 2H^{\oplus} + C_2O_4^{2-}$$

(Basicity = n-factor = 2)

$$Ew = \frac{M}{2}$$

$$NaHC_2O_4 \longrightarrow Na^{\oplus} + H^{\oplus} + C_2O_4^{2-} \text{ (Basicity = 1)}$$

$$Ew = \frac{M}{1}$$

(d → r)

When it behaves as reducing agent ($n = 2$) for both

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

$\therefore Ew = M/2$ (for both)

4. **(a → r)**

$$\overset{2+}{Fe}(C_2O_4^{2-}) + Fe_2(C_2O_4)_3 \xrightarrow[(n=5)]{MnO_4^{\ominus}} Mn^{2+} + Fe^{3+} + CO_2$$

$(n = 3)$ $(n = 6)$

Since 5 mol of $MnO_4^{\ominus}$ of equal M of FeC_2O_4 and $Fe_2(C_2O_4)_3$ is given, so moles of each = 2.5

1 Eq of $MnO_4^{\ominus}$ = 1 Eq of FeC_2O_4

$$\frac{1}{5}\text{ mol} = \frac{1}{3}\text{ mol}$$

Moles of $MnO_4^{\ominus} = 2.5 \times \frac{3}{5} = 1.5$

Similarly, for $Fe_2(C_2O_4)_3$, $(n = 6)$

Moles of $MnO_4^{\ominus} = 2.5 \times \frac{6}{5} = 3.0$

Total moles = 3.0 + 1.5 = 4.5

(b → s)

n factor for $Cr_2O_7^{2-} = 6$

Moles of $Cr_2O_7^{2-}$ for $Fe(C_2O_4)$ oxidation $= 2.5 \times \frac{3}{6} = 1.25$

Moles of $Cr_2O_7^{2-}$ for $Fe_2(C_2O_4)_3$ oxidation $= 2.5 \times \frac{6}{6} = 2.5$

Total moles = 1.25 + 2.5 = 3.75

(c → q)

$$\underset{n=6}{CuS} + \underset{n=8}{Cu_2S} \xrightarrow[(n=5)]{MnO_4^{\ominus}} Mn^{2+} + Cu^{2+} + SO_2$$

Moles of $MnO_4^{\ominus}$ for CuS oxidation $= 2.5 \times \frac{6}{5} = 3$

Moles of $MnO_4^{\ominus}$ for Cu_2S oxidation $= 2.5 \times \frac{8}{5} = 4$

Total moles = 3 + 4 = 7.

(d → t)

n factor for $Cr_2O_7^{2-} = 6$.

Moles of $Cr_2O_7^{2-}$ for CuS oxidation $= 6.0 \times \frac{6}{6} = 6.0$

Moles of $Cr_2O_7^{2-}$ for Cu_2S oxidation $= 6.0 \times \frac{8}{6} = 8.0$

Total moles = 6 + 8 = 14

(e → p)

$$\underset{(n=5)}{MnO_4^{\ominus}} + \underset{(n=6)}{Cr_2O_7^{2-}} \xrightarrow[(n=2)]{H_2O_2} Mn^{2+} + Cr^{3+} + O_2$$

Moles of H_2O_2 for $MnO_4^{\ominus}$ reduction $= 2.0 \times \frac{5}{2} = 5$

Moles of H_2O_2 for $Cr_2O_7^{2-}$ reduction $= 2.0 \times \frac{6}{2} = 6$

Total moles = 5 + 6 = 11

Numerical Value Type

1. **(4)** $\overset{+2}{Fe}\ \overset{-1\times 2}{S_2} \longrightarrow \overset{+3\times 2}{Fe_2}\ \overset{-2\times 3}{O_3} + \overset{+4\ -2\times 2}{SO_2}$

$$\left.\begin{matrix} \underset{2x=4}{2Fe^{2+}} \xrightarrow{0} \underset{2x=6}{Fe_2^{3+}} + 2e^- \end{matrix}\right] \quad n = \frac{2}{2} = 1$$

$$\left.\begin{matrix} \underset{2x=-2}{S_2^{2-}} \longrightarrow \underset{\substack{2x-8=0\\2x=8}}{2SO_2} + 10e^- \end{matrix}\right] \quad n = 10$$

Total n factor = 10 + 1 = 11

2. **(4)** $\underset{2x=6}{\overset{+3}{As_2}} \longrightarrow \underset{\substack{2x-16=-6\\2x=10}}{2AsO_4^{3-}} + 4e^-$

$$\underset{3x=-6}{S_3^{2-}} \longrightarrow \underset{\substack{3x-24=-6\\3x=18}}{3SO_4^{2-}} + 24e^-$$

$$As_2S_3 \longrightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 28e^-$$

3. **(2)** $3e^- + \underset{\substack{x-6=-1\\x=5}}{NO_3^{\ominus}} \longrightarrow \underset{\substack{x-2=0\\x=2}}{NO}$

4. **(3) i.** $\left[\begin{matrix} Fe^{2+} \longrightarrow Fe^{3+} + e^- \\ C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \end{matrix}\right] \quad (n = 3)$

ii. $Fe_2(C_2O_4)_3$, Fe^{3+} ion does not change.

$$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$$

5. **(4) i.** $\left.\begin{matrix} \overset{1+}{Cu_2} \longrightarrow 3Cu^{2+} + 2e^-\ (n = 2) \\ S^{2-} \longrightarrow SO_2 + 6e^-\ (n = 6) \end{matrix}\right] \quad (n = 8)$

ii. Cu^{2+} does not change only S^{2-} changes to SO_2 hence $n = 6$.

6. **(1)** Refer to Illustration 3.13.

$$8KI + \underset{(5\text{ mol})}{5H_2SO_4} \longrightarrow 4K_2SO_4 + 4I_2 + \underset{(1\text{ mol})}{H_2S} + 4H_2O$$

7. **(2)** 5.6 'V' of H_2O_2 = 1N $= \frac{M}{2}$

$$10\ 'V' \text{ of } H_2O_2 = \frac{11.2}{5.6 \times 2}\text{ M} = 1\text{ M}$$

8. **(4) i.** $10e^- + 2IO_3^{\ominus} \longrightarrow I_2$

$$2I^{\ominus} \longrightarrow I_2 + 2e^-] \times 5$$

$$\underset{2\text{ mol}}{2IO_3^{\ominus}} + \underset{10\text{ mol}}{10\ I^{\ominus}} \longrightarrow \underset{6\text{ mol}}{6I_2}$$

ii. $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{\ominus}$

1 mol 2 mol

1 mol of $IO_3^{\ominus}$ = 5 mol $I^{\ominus}$ ≡ 3 mol

I_2 = 6 mol of $S_2O_3^{2-}$

9. (1) 5.6 'V' H_2O_2 = 1N

$$10 \text{ '}V\text{' } H_2O_2 = \frac{10}{5.6} N$$

mEq of H_2O_2 = mEq of $MnO_4^{\ominus}$

$$\frac{10}{5.6} \times 112 \equiv 0.04 \times 5\ (n \text{ factor}) \times V$$

V ≡ 1000 ml = 1 L

10. (1) $10e^- + 2MnO_4^{\ominus} \longrightarrow 2Mn^{2+}\ (n = 5)$

Eq of $MnO_4^{\ominus}$ ≡ Eq of $Fe_2(C_2O_4)_3$

$(n = 5)$ $(n = 6)$

$$1\text{ L} \times \frac{M}{10} \times 10 \equiv \frac{1}{6}\text{L} \times 6 \times x$$

$x = 1\ M$

11. (1) $H_2O_2 + ClO_3^{\ominus} \longrightarrow [Cl_2 \text{ or } Cl^{\ominus} + O_2^0$

$2x = 0$

12. (4) $H_2O_2 + As_2O_3 \longrightarrow AsO_4^{3-} + H_2O^{2-}$ (oxidation number of O = –2)

13. (1) Mw of washing soda = 286, Mw of $CaCO_3$ = 100 g mol^{-1}

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

$$0.0286 \text{ g } Na_2CO_3{\cdot}10H_2O = \frac{0.0286}{286/2} \times 10^3 = 0.2 \text{ mEq}$$

$$0.2 \text{ mEq of } Na_2CO_3 = \frac{0.2}{2} \text{ mmol of } CaCO_3 \text{ in 1 L}$$

$= (0.1 \times 10^{-3}) \times 100$ g in 10^3 mL

$= 0.01$ g in 10^3 mL

$$\text{ppm} = \frac{0.01 \times 10^6}{10^3} = 10 \text{ ppm}$$

14. (2) $Mn^{2+} \longrightarrow MnO_2 + 2e^-$

$4e^- + O_2 \longrightarrow 2H_2O$

1 Eq of Mn^{2+} = 1 Eq of O_2

$(n = 2)$ $(n = 4)$

$\frac{1}{2}$ mol = 1 Eq

2 mol Mn^{2+} = 4 Eq of O_2

15. (3) H_2BO_3 is a weak monobasic acid (n factor = 1)

$N = n \times M = 1 \times 2 = 2$

16. (3) Eq of $KReO_4$ ≡ Eq of $MnO_4^{\ominus}$

$0.2 \times n = 1.6$ Eq

$$n = \frac{1.6}{0.2} = 8$$

Hence, there is an $8e^-$ reduction.

$$8e^- + \underset{x=7}{\overset{+7}{ReO_4^{\ominus}}} \longrightarrow \underset{x=-1}{Re^{-1}}$$

Oxidation state of Re = –1

17. (2) First part: mmoles of $Na_2S_2O_3$ used

= 8 × 2 × 1 (n-factor) = 16

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

1 mol 2 mol

$$\text{mmol of } I_2 \text{ used} = \frac{1}{2} \text{ mmol of } Na_2S_2O_3 = \frac{16}{2} = 8 \quad \text{...(i)}$$

Second Part: $3I_2 + 6NaOH \longrightarrow 5NaI + NaIO_3 + 3H_2O$

mmoles of H_2SO_4 = excess NaOH = 30 × 0.1 × 2 × (n-factor) = 6

mmol of total NaOH = 300 × 0.1 × 1 (n-factor) = 30

mmol of NaOH used = 30 – 6 = 24

$$\text{mmol of } I_2 \text{ used} = \frac{1}{2} \text{ mmol of NaOH used}$$

$$= \frac{24}{2} = 12 \text{ mmol of } I_2 \text{ used}$$

Total mmol of I_2 used = Part I + Part II

= 8 + 12 = 20 mmol

$$M \text{ of } I_2 = \frac{\text{mmol}}{V_{\text{mL}}} = \frac{20}{200} = \text{'0.1 M'}$$

20 times the initial $M_{I_2} = 0.1 \times 20 = 2$

Archives

JEE Advanced

Single Correct Answer Type

1. (2) $2MnO_4^{\ominus} + 5C_2O_4^{2-} + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

$x = 2, y = 5, z = 16$

Multiple Correct Answers Type

1. (1, 3, 4)

(1) In neutral or weak basic medium :

$$\overset{+7}{MnO_4^{\ominus}} + 3e^- \longrightarrow \overset{+2}{MnO_2}\ (n = 3)$$

(3) In strongly alkaline medium :

$$\overset{+7}{MnO_4^{\ominus}} + e^- \longrightarrow \overset{+6}{MnO_4^{2-}}\ (n = 1)$$

(4) In acidic medium :

$$\overset{+7}{MnO_4^{\ominus}} + 5e^- \longrightarrow Mn^{2+}\ (n = 5)$$

Linked Comprehension Type

1. (3) 1st Method :

m moles of hypo = 0.25 × 48 = 2 × m moles of Cl_2

$$\text{m moles of } Cl_2 = \frac{0.25 \times 48}{2}$$

= 6 m moles = m moles of Cl_2

= m moles of $CaOCl_2$

$$\text{So, molarity} = \frac{6}{25} \text{ M} = 0.24 \text{ M}$$

2nd Method :

'n' factor for $S_2O_3^{2-} = \frac{2}{2} = 1$ $(2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^{\ominus})$

'n' factor for I_2 and $Cl_2 = 2$

$(2e^{\ominus} + I_2 \longrightarrow 2I^{\ominus})$; $(2e^{\ominus} + Cl_2 \longrightarrow 2Cl^{\ominus})$

mEq of $S_2O_3^{2-} = 0.25$ N × 48 mL = 12

mEq of I_2 = mEq of $I^{\ominus}$ = mEq of $Cl_2 = 12$

m moles of $Cl_2 = \frac{\text{mEq}}{\text{'}n\text{' factor}} = \frac{12}{2} = 6$

$\therefore$ m moles of Cl_2 = m moles of $CaOCl_2 = 6$

$M \times V$ (mL) = m moles

$M = \frac{\text{m moles}}{V\text{ (mL)}} = \frac{6}{25\text{ mL}} = 0.24$ M

2. **(1)** $CaOCl_2 = Ca(OCl)\,Cl$

OCl : Hypochlorite ion, which is anion of HOCl

Anhydride of HOCl = Cl_2O

Numerical Value Type

1. **(6)** 30 mL of 0.01 M $[Cr(H_2O)_5Cl]Cl_2 \Rightarrow 2Cl^{\ominus}$ ions

$\therefore$ Number of $Cl^{\ominus}$ ions = 30 × 0.01 × 2 = 0.6 mmol

$\therefore$ mmoles of $Ag^{\oplus}$ ions required = 0.6 mmol

$\therefore$ Volume = ?

$V \times 0.1 = 0.6, \Rightarrow V = 6$ mL

2. **(5)** $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

3. **(6)**

i. In neutral or faintly alkaline medium:

$S_2O_3^{2-} + 5H_2O \longrightarrow 2HSO_4^{\ominus} + 8\bar{e} + 8H^{\oplus}$ ('n' factor = 8)

ii. In basic medium:

$S_2O_3^{2-} + 10\,\overset{\ominus}{O}H \rightarrow 2SO_4^{2-} + 5H_2O + 8\bar{e}$ ('n' factor = 8)

iii. In neutral or faintly alkaline medium:

$3\bar{e} + 4H^{\oplus} + MnO_4^{\ominus} \longrightarrow MnO_2 + 2H_2O$ ('n' factor = 3)

Eq of $MnO_4^{\ominus}$ = Eq of $S_2O_3^{2-}$ = Eq of $HSO_4^{\ominus}$.

$\frac{1}{3}$ moles of $MnO_4^{\ominus} = \frac{1}{8}$ moles of $S_2O_3^{2-}$

8 moles of $MnO_4^{\ominus}$ = 3 moles of $S_2O_3^{2-}$

Since 1 mol of $S_2O_3^{2-}$ produces 2 moles of $HSO_4^{\ominus}$

$\therefore$ 3 moles of $S_2O_3^{2-}$ = 6 moles of $HSO_4^{\ominus}$

Hence the value of X is 6.

4. **(2992)**

$$Ca(OH)_2 + (NH_4)_2SO_4 \longrightarrow 2NH_3 + \underset{\text{(Gypsum)}}{CaSO_4.2H_2O}$$

moles 12 $\frac{1584}{132} = 12$ 24 12

Weight of gypsum formed = 12 × 172 = 2064 g

$$NiCl_2.6H_2O + 6NH_2 \longrightarrow [Ni(NH_3)_6]Cl_2$$

moles $\frac{952}{238} = 4$ 24 $\frac{24}{6} = 4$

Mass of $[Ni(NH_3)_6]Cl_2$ formed = 4 × 232 = 928 g

Total weight = 2064 + 928 = 2992 g.

Chapter 4

Concept Application Exercises

Exercise 4.1

Objective Type

1. **(1)** $E = \frac{hc}{\lambda}, \therefore \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = \frac{4000}{2000} = 2$
2. **(2)** In Bohr's theory, while calculating the energy of electron, the potential energy has been found out by considering only the attraction between the electron and the nucleus. If there is another electron in the orbit the potential energy would change the electron–electron repulsion. Therefore, the Bohr's model is meant for all one-electron systems.
3. **(2)** Atomic number of Li^{2+} is 3

   $$\frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

   $$136800 = R_H \times 9 \left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

   $$R_H \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{136800}{9} = 15200$$
4. **(4)** $\Delta x \times \Delta p \geq h/4\pi$

   if $\Delta x = 0$, then Δp will be infinite
5. **(1)** $\lambda = \frac{h}{mv}$

   λ will be large if m is small.
6. **(4)** In Bohr's model, the energy levels are discrete and not continuous.

Exercise 4.2

Subjective Type

1. Three: principal quantum number, azimuthal quantum number, and magnetic quantum number.
2. The possible values of l are 0, 1, 2, 3, and 4.
3. The possible values of m are +3, +2, +1, 0, −1, −2, −3.
4. For *g* subshell, $l = 4$. The minimum value of n for which l can be 4 is 4 + 1 or 5. (The value of l can be 4 for $n = 5, 6, 7, ...$)
5. (1) 5*d* (2) 6*f* (3) 4*s* (4) 5*g*
6. 2.
7. $n = 3, l = 2, m_l = +2, +1, 0, -1, -2$
8. The largest value of m_l can be +3 when $l = 3$. $l = 3$ corresponds to *f* subshell. Therefore, the electron must be present in *f* subshell.
9. **a.** Not possible because n cannot be zero.

   c. Not possible because the value of l in this case is equal to n, which is not allowed.

   e. Not possible because the value of l in this case is equal to n, which is not allowed.
10. (1)For $n = 4$, 32 (2×4^2) electrons are possible out of which 16 can have $m_s = -1/2$.

    (2)$n = 3, l = 0$ corresponds to 3*s* subshell. It can accommodate only 2 electrons.
11. (1) 16 **b.** 7
12. (1) +1, 0, −1; **b.** +2, +1, 0, −1, −2.
13. Spherical shape.

    Difference between 1*s* and 2*s*

    a. 2*s* orbital is bigger in size.

    b. 2*s* orbital has more energy than 1*s* orbital.
14. **a.** For $n = 4$, l can have values 0, 1, 2, 3. Thus, there are four sub-shells in $n = 4$ energy level. These four sub-shells are 4*s*, 4*p*, 4*d*, and 4*f*.

    b. For $n = 4$, the number of orbitals is $= (4)^2 = 16$. Each orbital can have one electron with $m_s = -1/2$. Thus, there are 16 electrons in sub-shells having $n = 4$ and $m_s = -1/2$.
15. **a.** two **b.** one

Objective Type

16. **(3)**
17. **(4)** All 2*p* orbitals are degenerate.
18. **(3)**The orbital angular momentum of an electron is calculated as $\sqrt{l(l+1)}\,\frac{h}{2\pi}$.

    $$\sqrt{0(0+1)}\,\frac{h}{2\pi} = 0$$
19. **(2)***xz* and *yz* are planes with zero electron density for d_{xy} orbital.

Exercises

Single Correct Answer Type

1. **(3)** Atomic number

   $$= \frac{(\%\ \text{Abundance}) \times (\text{Isotope})_1 + \%\ \text{of}\ (\text{Isotope})_2}{100}$$
2. **(4)** Mass number is a whole number.
3. **(1)**
4. **(3)** $l = 1$, therefore *p* orbitals
5. **(3)** Isotones have same number of neutrons.

   ${}_{32}Ge^{76}$ $n = 76 - 32 = 44$

   i. ${}_{32}Ge^{77}$ $n = 77 - 32 = 45$

   ii. ${}_{33}As^{77}$ $n = 77 - 33 = 44$

   iii. ${}_{34}Se^{77}$ $n = 77 - 34 = 43$

   iv. ${}_{34}Se^{78}$ $n = 78 - 34 = 44$

   So answer is (3).
6. **(1)** $n_3 \rightarrow n_2$
7. **(3)** The limiting line of Balmer series refers to the transition from ∞ to 2nd orbit.

   $$\nu = 3.29 \times 10^{15} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) s^{-1}\ (n_1 = 2, n = \infty)$$

   $$= 3.29 \times 10^{15} \times \frac{1}{4} = 8.22 \times 10^{14}\ s^{-1}$$

8. (1) Meson

9. (4)

10. (1) $1s^2, 2s^2, 2p_x^1\ 2p_y^1\ 2p_z^1$ (Pauli's exclusion principle)

11. (4) $n \neq m$

12. (4) Spin does not give the orientation of electron cloud.

13. (4)

14. (3) $\frac{-1321}{4} - \left(\frac{1312}{1}\right) = 984$ kJ

15. (4) **16. (3)**

17. (2) For f orbital, $l = 3$, here $n = 2$

but $n < l$

18. (3) **19. (1)**

20. (2) ψ = wave function

21. (4)

22. (2) In X ; l = d

In Y, $l = s$

Energy of $d > s$

23. (1) $$\lambda = \frac{hc}{\Delta E} = \frac{6.62 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{m s}^{-1}}{E \times 1.602 \times 10^{-19}\ \text{J}}$$

$$= 12395 \times 10^{-10}\ \text{m}$$

24. (1) **25. (3)**

26. (3) $$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34}}{0.5 \times 100} = 1.324 \times 10^{-34} \times 10^{-1}$$

$$= 1.324 \times 10^{-35}\ \text{m}$$

27. (2) Lyman series

28. (3) $$\bar{\nu}_{\text{He}^{\oplus}} = \frac{1}{\lambda} = R \times 2^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R\left(\frac{4}{n_1^2} - \frac{4}{n_2^2}\right) \qquad \text{...(i)}$$

$$\bar{\nu}_{\text{H}_2^{\oplus}} = \frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \qquad \text{...(ii)}$$

Compare equations (i) and (ii), we get

$$\therefore\ \frac{1}{1^2} = \frac{4}{n_1^2},\ n_1^2 = 4,\ n_1 = 2$$

$$\frac{4}{n_2^2} = \frac{1}{2^2},\ n_2^2 = 16,\ n_2 = 4$$

$(4 \rightarrow 2)$

29. (3) KE = (Energy of radiation – Work function)

$$= \left(h \times \frac{c}{\lambda} - 4.2\right)$$

$$= \left(\frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{2000 \times 10^{-10}}\right) - (4.2 \times 1.602 \times 10^{-19})$$

$$= (9.9 \times 10^{-19}) - (6.7 \times 10^{-19}) = 3.2 \times 10^{-19}\ \text{J}$$

30. (2) $\text{KE} = h\nu_0 - h\nu_0$

$$h\nu_1 - h\nu_0 = 2(h\nu_2 - h\nu_0)$$

$$\nu_0 = 2(\nu_2 - \nu_1)$$

$$= 2(2.0 \times 10^{16}) - (3.2 \times 10^{16})$$

$$= 8 \times 10^{15}\ \text{s}^{-1} = 8 \times 10^{15}\ \text{Hz}$$

31. (4)

32. (4) s orbitals are independent of angular wave function. Thus, they do not have any angular node. They have only spherical node. The number of spherical nodes in s orbitals are given by $(n - 1)$, where n is the principal quantum number.

33. (3) $r = \frac{n^2 a_0}{z}$, (when $n = 1, Z = 1$)

$r_1 = a_0$

$r_2 = 4a_0$ (when $n = 2, Z = 1$)

$r_3 = 9a_0$ (when $n = 3, Z = 1$)

Hence, ratio is 1:4:9.

34. (2) $5f^{14}, 6d^3 \Rightarrow 17e^-$

$5f^{14} = (n + l) = 5 + 3 = 8$

$6d^3 = (n + l) = 6 + 2 = 8$

35. (3) Work function = Threshold energy

$$= h\nu_0 = \frac{hc}{\lambda_0}$$

$$= \frac{6.6 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{m}}{330 \times 10^{-9}\ \text{m}} = 6.6 \times 10^{-19}\ \text{J}$$

36. (1) Neutron

37. (3)

38. (2) Bohr can explain hydrogen-like elements.

39. (3) Electronic configuration of M^{2+}

$= 2 + 8 + 14 = 24e^-$

Since two e^- has been lost in forming M^{2+} ion from metal, so total number of protons should be = 24 + 2 = 26

Hence, number of neutrons = 56 – 26 = 30

40. (1) **41. (3)** **42. (1)**

43. (3) Hund's rule

44. (4)

45. (3) $l = 0$ or s orbital

46. (2) $s < p < d < f$

47. (3)

48. (2) Ni ($Z = 28$) or $3d^8 4s^2$

$\therefore\ \text{Ni}^{2+} = d^8$

49. (3) **50. (3)**

51. (4) Hund's rule

52. (4) **53. (1)**

54. (1) Angular nodes = 1,

Spherical nodes = $n - l - 1 = 3 - 1 - 1 = 1$

55. (1) $E_1 = h\nu_1 = h\frac{c}{\lambda_1} = \frac{hc}{2000}$

$E_2 = h\nu_2 = h\frac{c}{\lambda_2} = \frac{hc}{4000}$

$$\frac{E_1}{E_2} = \frac{hc \times 4000}{2000 \times hc} = 2$$

56. (1)

57. (1) $E_n = \dfrac{E \text{ for H} \times Z^2}{n^2} = \dfrac{-13.6 \times 1^2}{25} = -0.54 \text{ eV}$

58. (1) $\lambda = \dfrac{h}{mv} = \dfrac{6.6 \times 10^{-27} \text{ erg s}}{\dfrac{2}{N_A} \times 2.4 \times 10^5 \text{ cm s}^{-1}}$

$$\left(\text{Mass of 1 molecule of } H_2 = \frac{2}{6.02 \times 10^{23}}\right)$$

$$= \frac{6.6 \times 10^{-27} \times 6.02 \times 10^{23}}{2 \times 2.4 \times 10^5}$$

$$= 8.27 \times 10^{-9} \text{cm}$$

$$= 0.8 \times 10^{-8} \text{ cm} = 0.8 \text{ Å} \approx 1 \text{ Å}$$

59. (2)

60. (4) $\bar{\nu}_{H_2^{\ominus}} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right) = 15200 \text{ cm}^{-1}$

$$\bar{\nu}_{Li^{2+}} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 3^2 \times 15200$$

$$= 136800 \text{ cm}^{-1}$$

61. (3) $r_n = \dfrac{r_1 \text{ for H} \times n^2}{Z}$

$$= \frac{0.53 \text{ Å} \times 2^2}{1}$$

$$= 0.53 \times 4 \text{ Å} = 0.053 \times 4 \text{ nm}$$

$$= (1 \text{ Å} = 10^{-10} \text{ m}, 1 \text{ nm} = 10^{-9} \text{ m})$$

62. (1)

63. (1) Number of spectral lines from the ground state

$$= \frac{n(n-1)}{2} = \frac{5 \times 4}{2} = 10$$

64. (2) Number of spectral lines from n_1 to n_2

$$= \frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2} = \frac{(5-2+1)(5-2)}{2} = 6$$

65. (3) Longest λ or shortest E

1. $\dfrac{1}{\lambda} = R\left(\dfrac{1}{1} - \dfrac{1}{4}\right) = \dfrac{3R}{4} = 0.75R$
2. $\dfrac{1}{\lambda} = R \times Z^2\left(\dfrac{1}{3^2} - \dfrac{1}{4^2}\right) = R \times 9 \times \dfrac{7}{144} = 0.4375R$
3. $\dfrac{1}{\lambda} = R \times 2^2\left(\dfrac{1}{3^2} - \dfrac{1}{4^2}\right) = R \times 4 \times \dfrac{7}{144} = 0.194R$
4. $\dfrac{1}{\lambda} = R\left(\dfrac{1}{2^2} - \dfrac{1}{5^2}\right) = R \times \dfrac{21}{100} = 0.21R$

Lowest value of $1/\lambda$ or highest value of λ or lowest E is in (3).

66. (4) $E_i = \text{IE} + \text{KE}$

or

$E_1 = \text{Threshold } E \text{ (or) Work function} + \text{KE}$

$$\left(h\nu = h\nu_0 + \frac{1}{2}mu^2\right)$$

or

$$hn = hn_0 + \frac{1}{2}mu^2$$

$$\frac{1}{2}mu^2 = h(n - n_0) = h\,\Delta n \qquad \text{...(i)}$$

$$\left(\lambda = \frac{h}{mu}, \therefore u = \frac{h}{m\lambda}\right)$$

Substitute the value of u in equation (i)

$$\frac{1}{2}m \cdot \frac{h^2}{m^2\lambda^2} = h\,\Delta n$$

$$\frac{h}{2\lambda^2 m} = \Delta n$$

$$\therefore \lambda = \sqrt{\frac{h}{2m\,\Delta n}}$$

67. (3)

68. (3) Atomic number = 7

Structure is $1s^2, 2s^2, 2p^3$ $\boxed{1}\ \boxed{1}\ \boxed{1}$

$n = 3,$

Total spin $= \pm\dfrac{1}{2}n = \pm\dfrac{1}{2} \times 3 = \pm\dfrac{3}{2}$

Magnetic moment $= \sqrt{n(n+2)}$

$$= \sqrt{3(3+2)} = \sqrt{15} \text{ BM}$$

69. (1) Atomic structure = 24

Structure is $3d^5, 4s^1, n = 6$

Total spin $= \pm\dfrac{1}{2} \times 6 = \pm 3$

Magnetic moment $= \sqrt{n(n+2)} = \sqrt{6(6+2)}$

$$= \sqrt{48} \text{ BM}$$

70. (2) 2K, 8L, 9M, and 2N

$1s^2$ $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^1$ $4s^2$

(K means $n = 1$, L means $n = 2$
M means $n = 3$ N means $n = 4$)

Structure is $3d^1, 4s^2$

Atomic number 21

71. (1) Total number of s e^- in Q. 70 is

$1s^2 + 2s^2 + 3s^2 + 4s^2 = 8$

72. (2) Total number of p e^- in Q. 70

$2p^6 + 3p^6 = 12$

73. (1) Total number of unpaired d e^- in Q. 70

$3d^1 = 1$

74. (1) Total number of unpaired e^- in Q. 70

$3d^1 = 1, n = 1$

75. (3) Valency of element in Q. 70

Structure is $3d^1, 4s^2$

So, e^- can be excited form $4s$ and $3d$ both (since energy difference between $3d$ and $4s$ is very very small).

So, valency is +2 and +3 both.

76. (1) Vapour density = 46

Molecular weight = 92

So, compound is N_2O_4.

Total number of $e^- = 7 \times 2 + 8 \times 4 = 46$.

Total number of e^- in 1 mole = $46N_A$

77. (1) Follow same as in Q. 70, 72.

78. (3)

79. (1) ${}_4Be^7 + {}_{-1}e^0 \rightarrow {}_3Li^7$

So, atomic number = 3, mass number = 7.

80. (1) $$\bar{\nu}_{H_2^{\oplus}} = \frac{1}{\lambda_{H_2^{\oplus}}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{...(i)}$$

$$\bar{\nu}_{He^{\oplus}} = \frac{1}{\lambda_{He^{\oplus}}} = RZ^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$= R \times 4\left(\frac{1}{4} - \frac{1}{16}\right)$$

$$= R \times \left(\frac{4}{4} - \frac{4}{16}\right) = R \times \left(1 - \frac{1}{4}\right) \quad \text{...(ii)}$$

Comparing equations (i) and (ii)

$$\therefore \frac{1}{n_1^2} = 1, n_1 = 1$$

$$\frac{1}{n_2^2} = \frac{1}{4}, n_2 = 2$$

81. (2) H_α line of Balmer series means first line of Balmer series.

$n_1 = 2 \quad n_2 = 3$

$$\bar{\nu} = \frac{1}{\lambda_\alpha} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36}$$

$$\therefore \lambda_\alpha = \frac{36}{5R} = X$$

H_β line of Balmer series means, second line of Balmer series, $n_1 = 2, n_2 = 4$.

$$\bar{\nu} = \frac{1}{\lambda_\beta} = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3R}{16}$$

$$\therefore \lambda_\beta = \frac{16}{3R} = X$$

when $\frac{36}{3R} = X$

Then $\frac{16}{3R} = \frac{X \times 5R \times 16}{36 \times 3R} = \frac{80X}{108}$ Å

82. (1) Shortest $\bar{\nu}$ means shortest E and vice versa.

When, $n = 1, n_2 = 2$

$$\bar{\nu} = \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4}R$$

Longest $\bar{\nu}$ means longest E

When $n_1 = 1, n_2 = \infty$

$$\bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = R$$

83. (1) $$r_n = \frac{r_1 \text{ for H} \times n^2}{Z} = \frac{0.529 \text{ Å} \times n^2}{Z}$$

$$r_2 \text{ for } Li^{2+} = \frac{0.529 \times 2^2}{3} = \frac{0.529 \times 4}{3} \text{ Å}$$

84. (2) $$r_1 \text{ for } He^{\oplus} = \frac{0.529 \times 1^2}{2} = 0.264 \text{ Å}$$

85. (1) The magnitude of the charge should be smallest and other charges should be integral multiple of that smallest charge. So, in this problem, smallest charge is 2.30×10^{-15}, but other charges are not integral multiple of this charge.

So, smallest charge is 1.15×10^{-15} because other charges are integral multiple of this charge.

86. (3) Let x% of Cl^{37} and $(100 - x)$% of Cl^{35} be present in ${}_{17}Cl^{35.5}$

$$\therefore 35.5 = \frac{x \times 37 + (100 - x) \times 35}{100}$$

Solve for x,

$x = 25$

$\therefore$ % of $Cl^{37} = 25$

$\therefore$ % of $Cl^{35} = 75$

$\therefore$ Ratio is 1:3

87. (4) **88. (3)**

89. (1) If Aufbau rule is not followed, electronic configuration is K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$. Last electron is in $3d$ (instead of 4s), hence d block (but it is of s block).

90. (2) Fe^{2+}: $[Ar]3d^6$ unpaired electron = 0

Mn^{2+} : $[Ar]3d^5\ 4s^1$ unpaired electron = 2

Cr : $[Ar]3d^4\ s^2$ unpaired electron = 0

If Hund's rule is not followed.

91. (4) $\lambda = \frac{h}{mv}$ distance travelled in one second by velocity

$V = vcm = \lambda$

$$\lambda = \frac{h}{m\lambda} \Rightarrow \lambda^2 = \frac{h}{m} \Rightarrow \lambda = \sqrt{\frac{h}{m}}$$

92. (2) $$\left[\begin{aligned} &PE = -\frac{Ze^2}{r_n}, \; KE = \frac{1}{2}\frac{Ze^2}{r_n} \\ &E_{Total} = \frac{-Ze^2}{r_n} + \frac{1}{2}\frac{Ze^2}{r_n} = \frac{-Ze^2}{2r_n} \\ &E_{Total} = \frac{1}{2}PE \\ &KE = -\frac{1}{2}PE \end{aligned}\right]$$

$$\frac{KE}{PE} = \frac{1}{2}\frac{Ze^2}{r_n} \Big/ \frac{-Ze^2}{2r_n} = -\frac{1}{2}$$

93. (4) $\frac{\text{KE}}{E_{\text{Total}}} = \frac{1}{2}\frac{-Ze^2}{r_n} \Big/ -\frac{Ze^2}{2r_n} = -1$

94. (1) $\frac{\text{PE}}{E_{\text{Total}}} = \frac{-Ze^2}{r_n} \Big/ \frac{-Ze^2}{2r_n} = 2$

95. (1)

96. (1) $V_{H_2^{\oplus}} = \frac{2\pi Ze^2}{nh}$ or $V \propto \frac{Z}{n}$

$\therefore V_{H_2^{\oplus}} \propto 1\,(Z = 1, n = 1)$

$V_{Li^{2+}} \propto \frac{Z}{n} \propto \frac{3}{3} \propto 1\,(Z = 3, n = 3)$

Therefore, velocity of e^- in the third orbit of Li^{2+} is the same velocity of an e^- in the first orbit of H atom, i.e., V.

97. (1) E_n for $H_2^{\oplus} = \frac{E_1 \text{ for H} \times Z^2}{n^2}$

$E_1 = -13.6$ eV

The possible excited state values are:

$$E_2 = \frac{-13.6}{4} = -3.4 \text{ eV}$$

$$E_3 = \frac{-13.6}{9} = -1.5 \text{ eV}$$

$$E_4 = \frac{-13.6}{16} = -0.85 \text{ eV}$$

So, the value is only –3.4 eV.

98. (1)

99. (4) Shortest λ will be produced in the ion, which has high Z value.

Z for $H_2^{\oplus} = 1$, Z for $He^{\oplus} = 2$

Z for $D = 2$, Z for $Li^{2+} = 3$

100. (1)

101. (3) $\bar{\nu}_1 = \frac{1}{\lambda_1} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36}$

$$\lambda = \frac{36}{5R}$$

$$\bar{\nu}_2 = \frac{1}{\lambda_2} = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3R}{16}$$

$$\lambda_2 = \frac{16}{3R}$$

When $\frac{36}{5R} \rightarrow 656.1$ nm

$$\therefore \frac{16}{3R} \Rightarrow \frac{656.1 \times 5R \times 16}{36 \times 3R} = 486 \text{ nm}$$

102. (1) The energy of an electron in Bohr orbits of hydrogen atom is given by the expression

$$E_n = -\frac{\text{Constant}}{n^2}$$

where n takes only integral values. For the first Bohr orbit, $n = 1$, and it is given that

$E_1 = -13.6$ eV. Hence

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

Of the given values of energy, only –3.4 eV can be obtained by substituting $n = 2$ in the above expression.

103. (1, 4) Only the configuration of (1) and (4) follow Hund's rule.

104. (2) The element is chromium atom in the ground state.

105. (3) The de Broglie wavelength is

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ J s})}{(0.200 \text{ kg})\,\{5\text{m}/(60 \times 60 \text{ s})\}}$$

$$= 2.4 \times 10^{-30} \text{ m}$$

106. (4)

107. (2) **108. (1)** **109. (3)** **110. (2)**

111. (1) Ionisation potential of nitrogen is more that of oxygen. This is because nitrogen has more stable fully half-filled p orbitals.

112. (1) Electronic configuration of fluorine and neon are 2, 7 and 2, 8, respectively.

113. (4)

114. (4) ${}^2_1H$; ${}^3_1T$

115. (2) $r \approx 10^{-13}$ cm

116. (3)

(1) **False.** The configuration is $3d^5\, 4s^1$.

(2) **False.** The wavelength of gamma rays is of the order of 10^{-11} m.

(3) **True.** In hydrogen atom, the energy of an electron depends only on the principal quantum number of the orbital which it occupies.

(4) **False.** In xz-plane, there is no electron density if an electron occupies $3d_{x^2-y^2}$ orbital.

117. (3)

(1) **False.** The electronic configuration of Zn^{2+} (atomic number 30) is $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}$. There are no unpaired electrons, hence, it is diamagnetic.

(2) **False.** In β emission, the atomic number of daughter element is increased by 1, due to the basic conversion of neutron into proton in the nucleus.

(3) **True.** An α-particle is ${}^4_2He^{2+}$. Hence, atomic number and mass number of daughter element are decreased by 2 and 4, respectively.

(4) **False.** There will occur an increase in atomic number by 2.

$${}^{m}_{n}A \xrightarrow{-\beta} {}^{m}_{n+1}B \xrightarrow{-\beta} {}^{m}_{(n+2)}C$$

118. (2)

(1) **False.** The neutrino has zero charge and seems to have rest mass equal to zero. It is emitted along with the emission of a positron (positive charge of $+1e$ and mass equal to electron). For example

$${}^{19}_{10}\text{Ne} \rightarrow {}^{19}_{9}\text{F} + {}^{0}_{1}\text{e} + \text{V}$$

Antineutrino is emitted along with the emission of β-particle.

(2) **True.** The expression of magnetic moment is

$$\mu_m = \sqrt{n(n+2)}\ \mu_B$$

(3) **False.**

(4) **False.** The correct expression is

$$L = \sqrt{l(l+2)}\left(\frac{h}{2\pi}\right)$$

119. (2)

(1) **True.**

(2) **False.** The expression $m_s\left(\frac{h}{2\pi}\right)$ is that of z-component of angular momentum.

(3) **True.** The azimuthal quantum number has the value 0, 1, 2, ..., $(n-1)$.

(4) **True.** The expressions are

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2}\frac{Ze^2}{(4\pi\varepsilon_0)r}$$

$$\text{PE} = -\frac{Ze^2}{(4\pi\varepsilon_0)r}$$

120. (2)

(1) **False.** The correct statement is as under:

No two electrons in an atom can have the same values of all the four quantum numbers n, l, m, and m_s.

(2) **True.** The expressions are

$$\text{PE} = -\frac{Ze^2}{(4\pi\varepsilon_0)\,r}$$

$$E = \text{KE} + \text{PE}$$

$$= \frac{1}{2}\frac{Ze^2}{(4\pi\varepsilon_0)r} - \frac{Ze^2}{(4\pi\varepsilon_0)r} = -\frac{1}{2}\frac{Ze^2}{(4\pi\varepsilon_0)r}$$

(3) **False.** The expression of velocity is $v = \frac{1}{n}$ (constant)

(4) **False.** The expression of energy is $E = -\frac{1}{n^2}$ (constant)

121. (1)

(1) **True.** For ionisation, $n_2 = \infty$. Hence

$$\Delta E = R\left(\frac{1}{n_1^2}\right)$$

(2) **False.** The ionisation energy increases in proportion to the square of the positive charge in the nucleus as is evident from the expression

$$R = \frac{2\pi^2 m\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2}{h^3 c}$$

$$\Delta\tilde{E}_i = R$$

(3) **False.** The correct expression is $\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$.

(4) **False.** For a multi-electron atom, the energy of an orbital depends on both principal and azimuthal quantum numbers. The larger the value of $n + l$, the larger the energy. For the same value of $n + l$, the larger the value of n, the larger the energy.

122. (2)

(1) **True.**

(2) **False.** The angular momentum depends only on the azimuthal quantum number.

(3) **True.** (4) **True.**

123. (3)

(1) **True.** The number of orbitals for a given value l is equal to the permitted value of m which can take values 0, ±1, ±2, ..., ±l, at total of $2l + 1$ values.

(2) **True.**

(3) **False.** A diamagnetic atom has no unpaired electrons.

(4) **True.**

124. (3)

(1) **False.** The half-filled and fully-filled electronic configurations are more stable. It is due to the larger exchange energy.

(2) **False.** The symbol s stands for sharp—a term used in the characterisation of spectral lines. The symbols p, d, and f stand for principal, diffuse, and fundamental, respectively.

(3) **True.**

(4) **False.** The expression is $E = hc/\lambda$.
Hence, energy and wavelength are inversely related.

125. (4)

(1) **True.** (2) **True.** (3) **True.**

(4) **False.** Lyman spectral series lies in the ultraviolet region.

126. (4)

(1) **True.**

(2) **True.** See Fig. (i) on the next page.

(3) **True.** See Fig. (e) on the next page.

(4) **False.** See Fig. (h) on the next page.

127. (2)

(1) **False.** See Fig. (e) on the next page.

(2) **True.** See Fig. (g) on the next page.

(3) **True.** See Fig. (i) on the next page.

(4) **False.** Bosons does not follow Pauli exclusion principle.

128. (4)

(1) **True.** It is due to the fact that the electron interacts in different manner with the external magnetic field.

(2) **True.** This splitting is known as Zeeman effect.

(3) **True.**

(4) **False.** It decreases with increase in the value of atomic number as is evident from the expression

$$E = -\frac{1}{n^2}\left[\frac{2\pi^2 m\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2}{h^2}\right]$$

Multiple Correct Answers Type

1. **(1, 2, 3)**
2. **(1, 4)** In singly filled orbital electrons must align in one direction or they all must be spin-up (↑) or spin-down (↓).
3. **(2, 4)**
4. **(2, 4)** The possible energy values of the excited state for an electron must be integral, multiple to the ground state energy. In other words, energy absorbed or emitted must be integral multiple (Planck's theory).
5. **(2, 3)** Mn (atomic number = 25)

   Electronic configuration = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

   $3d^5 = \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

   Mn^{2+}

   Electronic configuration = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

   $3d^5 = \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$
6. **(2, 3)**
7. **(1, 2, 3)**

   Isotopes: Elements that contain same atomic number.
8. **(1, 2, 3, 4)**
9. **(1, 2, 3)**

   Isotones: Elements that contain same number of neutrons.
10. **(1)** Excited state is given as = $\frac{-13.6\text{ eV}}{n^2}$

    e.g., $n = 2$, $E = \frac{-13.6}{4} = -3.4$ eV
11. **(1, 3)** 12. **(1, 2, 3)** 13. **(1, 4)**
14. **(1)** According to $(n + l)$ rule

    for $2s$, $n = 2$, $l = 0$

    $\therefore n + l = 2$

    Similarly for $3d = (n + l) = 5$

    $4s = (4 + 0) = 4$

    $5f \rightarrow 5f = (5 + 3) = 8$

    $\therefore$ $2s$ is lower in energy.
15. **(1, 2)** Order of energies of different orbital is $s < p < d < f$.
16. **(1, 2)** Angular momentum = $\sqrt{l(l+1)}\,\frac{h}{2\pi}$

    For d electron, $l = 2$

    $\therefore$ Angular momentum = $\sqrt{2\,(2+1)}\,\frac{h}{2\pi} = \sqrt{6}\cdot\frac{h}{2\pi}$

    or $\hbar = \frac{h}{2\pi}$

    $\therefore$ Angular momentum = $\sqrt{6}\cdot\hbar$
17. **(2, 3)** Same as in Q. 16.
18. **(2, 4)** Angular quantum number (l) may have value less than the principal quantum number.

    i.e., $l < n$

    (1) $4f$: $n = 3$, $l = 3$

    (3) $2d$: $n = 2$, $d = 2$
19. **(4)** It corresponds to $3p$ (3), $3d$ (5), $4s$ (1), $4p$ (3), $5s$ (1) = 13
20. **(1, 2, 4)**
21. **(2, 3, 4)**
22. **(2)** For H atom, first Balmer line in series is

    $$E_3 - E_2 = \frac{-E_1(H)}{(3)^2} - \frac{E_1(H)}{(2)^2} = \frac{5E_1(H)}{36}$$

    For $He^{\oplus}$ ion ($Z = 2$)

    $$E_6 - E_4 = -\frac{E_1(H)\times(2)^2}{6^2} - \frac{E_1(H)\times(2)^2}{4^2}$$

    $$= -E_1(H)\times 2^2\left|\frac{16-36}{16\times 36}\right|$$

    $$= \frac{4\times 20}{36\times 16}E_1(H) = \frac{5E_1(H)}{36}$$
23. **(2, 3, 4)** 24. **(1, 2)**
25. **(3)** Number of nodes = $n - l - 1 = 4 - 0 - 1 = 3$
26. **(1, 2, 3)**
27. **(1, 2) Exp:** Number of dark lines (in absorption), i.e., excitation = Number of bright lines (in emission), i.e., de-excitation

    It is possible only when the e^- is excited to $n = 2$ from ground state.

    Clearly, $\Delta E = 91.8$ eV and 40.8 eV are possible.

    (Li^{2+}) ($He^{\oplus}$)
28. **(3)** V: 3 unpaired electrons $\Rightarrow x$

    Cr: 6 unpaired electrons $\Rightarrow y$

    Mn : 5 unpaired electrons $\Rightarrow z$

    $\therefore\ y > z > x$
29. **(2)** Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$ ($Z = 24$ for Cr)

    $l = 1 \Rightarrow p$ orbital $\Rightarrow$ 12 electrons

    $l = 2 \Rightarrow d$ orbital $\Rightarrow$ 5 electrons
30. **(1)** $\nu = \frac{c}{\lambda} = RcZ^2\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) = RcZ^2\left(\frac{1+2n}{n^2(n+1)^2}\right)$

    $\approx RcZ^2\,\frac{(2n)}{n^4} \propto n^{-3}$
31. **(3)** Third highest energy between : $n = 5$ and $n = 1$ $\Rightarrow 3 \rightarrow 1$.
32. **(1, 2, 3)** Refer to Rutherford's atomic experiment.
33. **(1, 2, 4)**
34. **(2, 3, 4)**
35. **(1, 2, 3)** In d, $n = l$, i.e., 3, but $l \neq n$.
36. **(1, 2)**
37. **(2, 3)** Heisenberg principle is only for microscopic particles which are moving with very high speed.
38. **(2, 4)**

    $n = 4$ (principal shell)

$m = -2$

$s = +1/2$

39. (1, 2) **40.** (1, 2, 3) **41.** (1, 2, 3)

42. (1, 2, 3) **43.** (1, 2, 3) **44.** (1, 2, 3, 4)

45. (1, 2, 3, 4)

Linked Comprehension Type

1. **(1)** Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$. Three electrons in $3d$ sub shell are unpaired.

2. **(2)** 2 electrons in $3s$, 2 electrons in $3p$, and 1 electron in $3d$ have $m_l = 0$.

3. **(4)** **4. (2)** **5. (4)**

The electronic configuration of an atom with 2K, 8L, and 5M electrons is:

$$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$$

6. **(3)** Atomic number = Number of electrons = 15

7. **(1)** Number of electrons in valence shell = 2 + 3 = 5

8. **(2)** Number of unpaired electrons = 3 $(3p_x^1\ 3p_y^1\ 3p_z^1)$

9. **(2)** Number of electrons having $n + l = 3$, i.e., in $3s$ and $2p$ orbitals = 2 + 6 = 8

10. **(3)** Maximum number of electrons having same spin = 9

11. **(3)** In $H_{1\to 2}$, the excitation energy = 10.2 eV.

When H atoms transfer their excitation energy (10.2 eV) to the electron in $He^{\oplus}$ is further excited to say $n = n_2$, thus $10.2 = 13.6 \times 2^2 \times \{1/2^2 - 1/n_2^2\}$, therefore, $n_2 = 4$.

12. **(3)** Visible region transition lies in Paschen series ($He^{\oplus}$ ion spectrum) 4→3 is the transition in visible region for $He^{\oplus}$ ion.

Therefore, $1/1 = R \times 2^2 \times \{1/3^2 - 1/4^2\}$

On solving, we get

$\lambda = 36/7 \times 1/R = 4689$ or closed is 4800 Å.

13. **(1)** $(PE)_{H\ atom}/(PE)_{He^{\oplus}\ ion} = 2(E_2)_{H\ atom}/2(E_2)_{He^{\oplus}\ ion}$

$= (Z^2/n^2)H/(Z^2/n^2)He^{\oplus}$

$= 1^2/2^2 = 1/4$

14. **(3)** Ground state electron in H atom can only be excited by energy greater than 10.2 eV. Thus, 15 eV photon energy will ionise the atom and 8.4 eV photon will not be able to excite the electron at all. Only 12.09 eV excite to higher states. Now, this will be excited to $n = 3$. During de-excitation, correspondence to three transitions: wavelength will be emitted.

−0.85 eV .... $n = 4$

−1.51 eV .... $n = 3$

−3.4 eV .... $n = 2$

−13.6 eV .... $n = 1$

15. **(1, 2, 4)** As electron from higher to lower orbit: $En\downarrow$ hence $KEn\uparrow$ [KE = En]

Similarly $PEn\downarrow$ [$PEn = 2En$]

Angular momentum $(L) = nh/2\pi$,, hence L↓ as $n\downarrow$

$\lambda_e = h/mv_n$ [$KEn\uparrow$ hence $Vn\uparrow$], therefore $\lambda_e\downarrow$

16. **(2)** PE_n (magnitude) $\propto m_\pi - \dfrac{Z^2}{n^2}$ $(= 2E_n)$

17. **(2)** Number of waves = Shell number = 4

18. **(4)** $3 \to 1 \Rightarrow \dfrac{h}{\lambda} = (2.18 \times 10^{-18} \times 273) \times Z^2 \times \left(\dfrac{1}{1^2} - \dfrac{1}{3^3}\right)$

$\Rightarrow \lambda$ depends on Z^2.

19. **(1)** $\lambda_\pi = \dfrac{h}{mV_{\pi^\ominus}} \propto \dfrac{n}{Zm_{\pi^\ominus}} \left[\because V_{\pi^-} \propto \dfrac{Z}{n}\right]$

20. **(4)** $Z = 3$

21. **(2)** $n = 6$

$n \longrightarrow 2$: $\Delta E = 10.2 + 17 = 27.2$ eV

$n \longrightarrow 3$: $\Delta E = 4.25 + 5.95 = 10.2$ eV

$$\left.\begin{aligned}&\Rightarrow 27.2 = 13.6Z^2\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\\ &\text{and } 10.2 = 13.6Z^2\left(\frac{1}{3^2} - \frac{1}{n^2}\right)\end{aligned}\right\} \Rightarrow Z = 3 \text{ and } n = 6$$

22. **(1)** Visible

23. **(1)** Li^{2+}

24. **(4)** $Z_x = 12$

25. **(1)** $Z_y = 10$

$$\sqrt{\nu} = 4.9 \times 10^7 (Z - 0.75) \Rightarrow Z = \frac{\sqrt{\nu}}{4.9 \times 10^7} + 0.75$$

[You will get to know about this]

For $\lambda = 9.87$ Å $\Rightarrow \nu = \dfrac{c}{\lambda} = \dfrac{3 \times 10^8}{9.87 \times 10^{-10}} = 0.3 \times 10^{18}$

$$\Rightarrow Zx = \frac{\sqrt{0.3 \times 10^{18}}}{4.9 \times 10^7} + 0.75 = 12$$

For $\lambda = 14.6$ Å $\Rightarrow \nu = \dfrac{3 \times 10^8}{14.6 \times 10^{-10}} = 0.2 \times 10^{18}$

$$\Rightarrow Z_y = \frac{\sqrt{0.2 \times 10^{18}}}{4.9 \times 10^7} + 0.75 = 10$$

26. **(1)** $\Delta x \cdot \Delta p \ge \dfrac{h}{4\pi} \Rightarrow \Delta p \ge \sqrt{\dfrac{h}{4\pi}}$ [$\because \Delta x = \Delta p$ (given)]

$\Rightarrow \Delta v \ge \dfrac{1}{m}\sqrt{\dfrac{h}{4\pi}} = 8 \times 10^{12}$ ms^{-1} [$\because \Delta p = m\,\Delta v$]

27. **(2)** $\Delta v = 2$ cm s^{-1} = 2×10^{-2} m s^{-1}

$\Delta x \cdot m\,\Delta v \ge \dfrac{h}{4\pi} \Rightarrow \Delta x \ge \dfrac{h}{4\pi} \times \dfrac{1}{m\,\Delta v}$

$$\Delta x = \frac{6.626 \times 10^{-34}}{4\pi \times 10^{-3} \times 2 \times 10^{-2}} = 2.64 \times 10^{-30} \text{ m}$$

28. **(2)** $2s$, $2p$ **29.** **(3)** Cr

30. **(1)** $_{19}$K **31.** **(1)** $_{29}$Cu

32. **(1)** Cr, Mo

33. **(1)** R **34.** **(1)** 3

35. **(1)** $\frac{119}{8R}$ **36.** **(3)** $8R_H$

37. **(4)** 3, 3 **38.** **(4)** 25

39. **(1)** 3/3 **40.** **(3)** $3d$

41. **(1)** $2s < 5p < 3p < 4d$

42. **(4)** **43.** **(2)** **44.** **(3)**

45. **(4)** **46.** **(3)**

47. **(1)** (1) It does not involve any change in the value of l. Value of l should change by ±1.

(2) There will be no change in angular momentum, because photons have angular momentum

(3) Δm for $4s$ and $3s$ is zero.

(4) Wavelength of electron wave are not the same because n value is difference.

48. **(4)** Maximum allowed value of $l = 4$ for $n = 5$,

$$\therefore l = \sqrt{4(4+1)}\frac{h}{2\pi} = \sqrt{20}\frac{h}{2\pi}$$

Matrix Match Type

1. **(a → t; b → p; c → s; d → r)**
2. **(a → r; b → s; c → p; d → t; e → q)**
3. **(a → t; b → s; c → p; d → q; e → r)**
4. **(a → q; b → r; c → r; d → p; e → s)**
5. **(a → u; b → s; c → p; d → q; e → t)**
6. **(a → r; b → p; c → q; d → s)**
7. **(a → r; b → p; c → q; d → s)**
8. **(a → r)**

Cr (atomic number = 24) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Half-filled d orbital is more stable due to greater symmetry and exchange energy.

(b → s)

Cu (atomic number = 29) – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Full-filled d orbital is more stable due to greater symmetry and exchange energy.

(c → q)

Fe (atomic number = 26) – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Fe^{3+} (23) – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

(a → r)

Hence, number of unpaired electrons are 5.

9. **(a → p; b → q; c → r; d → s)**
10. **(a → q; b → r; c → p; d → s)**
11. **(a → p; b → s; c → r; d → q; e → t)**
12. **(a → s; b → r; c → q; d → p)**
13. **(a → t; b → s; c → r; d → q; e → p)**

Total spin, $s = \sqrt{n(n+2)}$

where n = number of unpaired electrons.

14. **(a → q, r, s)**

$n_1 \rightarrow n_\infty$ in H atoms:

- UV region (Lyman series)
- $\Delta E = \frac{hc}{\lambda} = hcR \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = hcR$

(Rydberg energy)

- Ionisation energy

(b → s)

$n_4 \rightarrow n_2$ in $He^{\oplus}$ ion:

- UV region (check yourself)

(c → r, s)

$n_\infty \rightarrow n_1$ in $He^{\oplus}$ ion:

- UV region (check yourself)
- Corresponding to Ionisation energy

(d → p)

$n_4 \rightarrow n_2$ in ion

- Visible region (Balmer series)

15. **(a → p, s)**

Angular momentum $(L) = \frac{nh}{2\pi} \Rightarrow L\uparrow$ as $n\uparrow$ and $L\downarrow$; $\uparrow$ as $n\downarrow$.

(b → r)

$KE_n = -E_n \propto \frac{Z^2}{n^2} \Rightarrow KE_n\uparrow$ as $Z\uparrow$; $\downarrow$ as $Z\downarrow$; $\uparrow$ as $n\downarrow$; $\downarrow$ as $n\uparrow$.

(c → p, r, s)

$PE_n = 2E_n \propto \frac{Z^2}{n^2} \Rightarrow PE_n\downarrow$ as $Z\uparrow$; $\uparrow$ as $Z\downarrow$; $\downarrow$ as $n\downarrow$; as $n\uparrow$.

(d → q)

$V_n \propto KE_n$ (Same behaviour as KE_n)

16. **(a → p, q; b → q; c → r; d → s)**
17. **(a → r, s; b → p, q; c → r, s; d → r, s)**
18. **(a → q; b → s; c → r; d → p)**
19. **(a → p; b → q; c → r; d → s; e → t)**
20. **(a → f; b → q; c → r; d → s)**
21. **(a → p; b → q; c → r; d → s; e → t)**
22. **(a → p; b → q; c → r; d → s)**
23. **(a → p; b → q; c → r; d → s; e → t)**

Numerical Value Type

1. **(2)** **2.** **(2)** **3.** **(2)** **4.** **(2)**

5. **(1)** (1) He = $1s^2$; $n = 1$; $l = 0$; $m = 0$; $s = 1/2, -1/2$

Sum $= 1 + \frac{1}{2} - \frac{1}{2} = 1$

6. **(3)** (Maximum two electrons)

7. **(3)** S_2, *i.e.*, $3p$

for p orbital l = 1 1.

8. **(3)**

$1p$ is not possible because $n = l = 8$.

3 f is not possible because $n = l = 3$.

9. (2) $Fe^{2+} = [Ar]3d^6$ $\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$ $n = 4$, $\mu = \sqrt{n(n+2)}$ BM

$Mn^{2+} = [Ar]3d^5$ $\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$ $n = 5$, $\mu = \sqrt{24}$ BM

$Cr^{2+} = [Ar]3d^4$ $\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{}$ $n = 4$, $\mu = \sqrt{35}$ BM

$Ni^{2+} = [Ar]3d^8$ $\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$ $n = \mu = \sqrt{8}$ BM

10. (1) Number of nodes $= n - l - 1 = 3 - 1 - 1 = 1$

11. (3)

$$\Delta E = 13.6 \times l^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 12.09 \text{ eV}$$

This will be only absorbed, rest is useless (unabsorbed) so, from $n_2 = 3$ to $n_1 = 1$, we have λ corresponding to $3 \rightarrow 2$; $2 \rightarrow 1$, and $3 \rightarrow 1$. So, total true spectral lines are 3.

Archives

JEE Main

Single Correct Answer Type

1. (3) By Heisenberg's uncertainty principle

$$\Delta x(m\Delta V) = \frac{h}{4\pi}$$

$$\Delta V_{acc} = 0.005\%$$

Or $\Delta V = \dfrac{600 \times 0.005}{100} = 0.03 \text{ ms}^{-1}$

$$\Delta x \times 9.1 \times 10^{-31} \times 0.03 = \frac{6.6 \times 10^{-34}}{4 \times 3.14}$$

Hence, $\Delta x = \dfrac{6.6 \times 10^{-34}}{4 \times 3.14 \times 0.03 \times 9.1 \times 10^{-31}}$

$$= 1.92 \times 10^{-3} \text{ m}$$

2. (2) $\lambda = \dfrac{h}{mV} = \dfrac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^3} = 3.97 \times 10^{-10}$ m

$$\approx 0.40 \text{ nm}$$

3. (4) Energy required for 1 Cl_2 molecule

$$= \frac{242 \times 10^3}{N_A} \text{ J}$$

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^{23}}{242 \times 10^3}$$

$$= 494 \times 10^{-9} \text{ m} = 494 \text{ nm}$$

4. (2) $IE = -E_1$

E_1 for $He^+ = -19.6 \times 10^{-18}$ J/atom

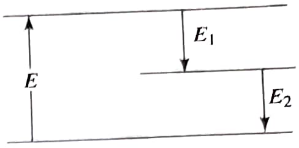
$$\frac{(E_1)_{He^+}}{(E_1)_{Li^{2+}}} = \frac{(Z_{He^+})^2}{(Z_{Li^{2+}})^2}$$

$$\frac{-19.6 \times 10^{-18}}{(E_1)_{Li^{2+}}} = \frac{4}{9}$$

Or $E_{1(Li^{2+})} = \dfrac{-19.6 \times 9 \times 10^{-18}}{4} = -4.41 \times 10^{-17}$ J/atom.

5. (3) Energy values are always additive.

$$E_{total} = E_1 + E_2$$



$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

$$\therefore \frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\frac{1}{355} = \frac{1}{680} + \frac{1}{\lambda_2}$$

$$\lambda_2 = 742.77 \text{ nm} = 743 \text{ nm}$$

6. (2) $\Delta E = hu = \dfrac{2\pi^2 mZ^2e^4k^2}{h^2}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

If electron falls from n_2-level to n_1-level

∴ In He^+, for $n_2 = 4$ to $n_1 = 2$ transition

$$\nu_{He+} = \text{Constant } (4)\left[\frac{1}{2^2} - \frac{1}{4^2}\right]\left[\because Z_{He^2} = 2\right]$$

$$= \text{Constant } \times 4\left[\frac{3}{16}\right] = \frac{3}{4} \times \text{constant}$$

$$\nu(H) = \text{Constant } (1)^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = \text{Constant} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

(1) For $n_2 = 3$ and $n_1 = 1$.

$$\nu(H) = \text{Constant}\left[\frac{1}{1} - \frac{1}{9}\right] = \frac{8}{9} \text{ Constant} \neq \frac{3}{4} \times \text{Constant}$$

(2) For $n_2 = 2$ and $n_1 = 1$.

$$\nu(H) = \text{Constant} \times \left[\frac{1}{1} - \frac{1}{4}\right] = \frac{3}{4} \text{ Constant} = \nu(He^+)$$

(3) For $n = 3$ and $n_1 = 2$

$$\nu(H) = \text{Constant} \times \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5}{36} \times \text{Constant} \neq \nu(He^+)$$

(4) For $n_2 = 4$ and $n_1 = 3$

$$\nu(H) = \text{Constant} \times \left[\frac{1}{3^2} - \frac{1}{4^2}\right] = \frac{7}{144} \text{ Constant} \neq \nu(He^+)$$

7. (2)

	n	l	n_l (suborbit)	n + l
(1)	4	1	$4p$	5
(2)	4	0	$4s$	4
(3)	3	2	$3d$	5
(4)	3	1	$3p$	4

Higher the value of $(n + l)$, higher is the energy. If $(n + l)$ are the same, then suborbit with lower value of n has lower energy. Thus,
$3p < 4s < 3d < 4p$
(4) < (2) < (3) < (1)

8. (1)

Energy change

$$\Delta E = 2.178 \times 10^{-18}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{hc}{\lambda}$$

$$= 2.178 \times 10^{-18}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= \frac{6.62 \times 10^{-34} \times 3.0 \times 10^{8}}{\lambda}$$

$\therefore \lambda \approx 1.214 \times 10^{-7}$ m

9. (1) The electronic configuration of rubidium atom ($Z = 37$) is given by

Rb = [Kr] $5s^1$

Hence, the quantum number for $5s^1$ electron is given by

$n = 5$

$l = 0$

$m = 0$

$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

10. (2) $(E_n)_H = -13.6 \dfrac{1^2}{n^2}$ eV

$n = 2 \Rightarrow E_2 = -3.4$ eV

11. (1) As electron of charge 'e' is passed through 'V' volt, kinetic energy of electron becomes = 'eV'

As wavelength of e^- wave $(\lambda) = \dfrac{h}{\sqrt{2\text{m.K.E.}}}$

$$\lambda = \frac{h}{\sqrt{2\text{meV}}}$$

$$\therefore \quad \frac{h}{\lambda} = \sqrt{2\text{meV}}$$

12. (4) $r_n = r_0 \times \dfrac{n^2}{Z}$; n = orbit number, Z is nuclear charge

$n = 2, z = 1$

$r_2 = 0.529 \times 4 = 2.126$ Å

JEE Advanced

Single Correct Answer Type

1. (2) Atomic mass of iron $= \dfrac{(5 \times 54) + (90 \times 56) + (5 \times 57)}{100}$

$= 55.95$

2. (2)

$$E \propto \frac{Z^2}{n^2}$$

$$r_n = \frac{r_1 \text{ for } H \times n^2}{Z}$$

$$r_n \propto n^2$$

$$r_n \propto (2)^2 a_0 \qquad (r_n = a_0)$$

$$r_n \propto 4a_0$$

$$mvr \propto \frac{nh}{2\pi} = \frac{2}{2}\frac{h}{\pi}$$

$$\therefore \quad v = \frac{h}{\pi\, mr} \qquad (r = a_0)$$

$$= \frac{h}{\pi\, m\, a_0} = \frac{h}{\pi m \times 4a_0}$$

So, $\text{KE} = \dfrac{1}{2}mv^2$

$$= \frac{1}{2}m\left(\frac{h}{4\pi \times ma_0}\right)^2 = \frac{h^2}{32\pi^2 ma_0^2}$$

3. (2) Na $\underset{\Delta H = -5.1\,\text{eV}}{\overset{\Delta H = +5.1\,\text{eV}}{\rightleftharpoons}}$ $\text{Na}^{\oplus} + e^{\ominus}$, here the backward reaction releases same amount of energy and known as **Electron gain enthalpy.**

Energy in 1st excited state = –3.4 eV.

4. (4)

The probability distribution curve for 1s $\bar{e}$ of H-atom is as shown in fig. (4).

Linked Comprehension Type

1. (2) The number of radial nodes is $n - l - 1$. For S_1, radial nodes = 1 and spherical (given). This means s orbital, so $l = 0$.

$n - l - 1 = 1$

$n - 0 - 1 = 0$

$n = 2$, this means S = $2s$

2. (3) $E_n = \dfrac{-13.6}{n^2} Z^2$

For ground state of H atom,

$$E_H = \frac{-13.6}{1^2} \times 1^2$$

For $2s$ of Li^{2+}

$$E_{Li^{2+}} = \frac{-13.6}{2^2} \times 3^2$$

$$\frac{E_{Li^{2+}}}{E_H} = \frac{\frac{-13.6}{4} \times 9}{-13.6} = 2.25$$

or $\quad E_{Li^{2+}} = 2.25 E_H$

3. (2) S_2 has one radial node.

$E_{S_2} = E_H$ (given)

or $\dfrac{-13.6}{n^2} \times 2^2 = \dfrac{-13.6}{1^2} \times 1^2$

or $n = 3$

Radial nodes = $n - l - 1 = 1$

or $3 - 1 - 1 = 1$

or $l = 1$

This means S_2 is $3p$.

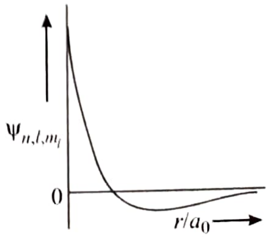
The orbital angular momentum quantum number means azimuthal quantum number which is 1 in this case.

Matrix Match Type

1. (1)

2s orbital – One radial node ($n - l - 1$)

(II) (ii)



2. **(3)**

1s orbital can not have θ function (angular function). Therefore D is incorrect.

3. **(4)**

For H-atom:

$$1s \text{ orbital} - \psi_{nlm} \propto \underset{\text{(i)}}{\left(\frac{Z}{a_0}\right)^{3/2}} e^{-\left(\frac{Zr}{a_0}\right)}, \text{S}$$

$$E_4 - E_2 = -\frac{13.6}{16} - \left(-\frac{13.6}{4}\right) = \frac{3 \times 13.6}{16}$$

$$E_6 - E_2 = -\frac{13.6}{36} - \left(-\frac{13.6}{4}\right) = \frac{8 \times 13.6}{36}$$

$E_4 - E_2$ is $\frac{27}{32}$ times of $E_6 - E_2$

merical Value Type

1. **(9)**

$n = 3 \Rightarrow l = 0, 1, 2$

for $l = 0$, $m = 0 \Rightarrow m_s = -1/2$ and $+1/2$

for $l = 1, m = -1 \Rightarrow m_s = -1/2$ and $+1/2$

$0 \Rightarrow m_s = -1/2$ and $+1/2$

$-1 \Rightarrow m_s = -1/2$ and $+1/2$

for $l = 2$, $m = -2 \Rightarrow m_s = -1/2$ and $+1/2$

$-1 \Rightarrow m_s = -1/2$ and $+1/2$

$0 \Rightarrow m_s = -1/2$ and $+1/2$

$1 \Rightarrow m_s = -1/2$ and $+1/2$

$2 \Rightarrow m_s = -1/2$ and $+1/2$

Alternatively $n = 3$

∴ Number of electrons $= 2n^2 = 2 \times 3^2 = 18$

Number of electrons with $m_s = -\frac{1}{2} = \frac{18}{2} = 9$

2. **(4)**

Since the value of $hc = 1240$ eV nm

Energy corresponding to $\lambda = 300$ nm is

$$\frac{1240 \text{ eV nm}}{300 \text{ nm}} = 4.134 \text{ eV}$$

Elements having $\phi < 4.134$ eV will show photoelectric effect, are Li, Na, K, and Mg $\Rightarrow \boxed{4}$

So, number of metals showing photo-electric will be four, i.e., Li, Na, K, and Mg.

3. **(5)**

$$\text{Since, } \lambda = \frac{h}{mv} = \frac{h}{2M\,\text{K.E.}} \quad \left(\begin{array}{c} \text{KE} = \frac{1}{2}mv^2 \\ 2\text{KE} = mv \end{array}\right)$$

$$\Rightarrow \lambda \propto \frac{1}{\sqrt{\text{MT}}} \quad (\text{since K.E.} \propto \sqrt{\text{T}})$$

For two gases

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \sqrt{\frac{M_{Ne}T_{Ne}}{M_{He}T_{He}}} = \sqrt{\frac{20}{4} \times \frac{1000}{200}} = 5$$

4. **(6)**

$|m_l|$ means both +1 and –1 values.

$4p \rightarrow 2e^{\ominus}$ $\quad$ $4\text{d} \rightarrow 2e^{\ominus}$ $\quad$ $4\text{f} \rightarrow 2e^{\ominus}$

5. **(3)**

Chapter 5

Concept Application Exercises

Exercise 5.1

1. For one mole of ideal gas, the kinetic gas equation is

$$PV = \frac{1}{3}mu^2 = \frac{1}{2} \times \frac{2}{3} mu^2 = \frac{2}{3} \times \frac{1}{2} mu^2$$

$$\text{or } P = \frac{2}{3}\left(\frac{1}{2}\frac{mu^2}{V}\right) = \frac{2}{3}E$$

2. Volume occupied by 1 mol of O_3 at 20°C and 82 mm pressure is calculated by applying general gas equation.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{76 \times 22400 \times 293}{273 \times 82} = 22281.92 \text{ cm}^3$$

$$\text{Now, } u = \sqrt{\frac{3PV}{Mo_3}}$$

$$u = \sqrt{\frac{3 \times 82 \times 13.6 \times 981 \times 22281.92}{48}}$$

$$= 3.90 \times 10^4 \text{ cm s}^{-1}$$

3. We know $Z = \frac{PV}{nRT}$ and $d = \frac{PMw}{RT}$

$$\therefore Z = \frac{PV}{nRT} = \frac{PV}{(m/w)RT} = \frac{MwPV}{wRT}$$

Since, $d = \frac{w}{V}$

$$\therefore Z = \frac{MP}{dRT} = \frac{(18 \times 10^{-3}) \times 10^5}{0.6 \times 8.31 \times 373.15} = 0.967$$

4. Calculation of ideal volume (V_{ideal})

$$V_{\text{ideal}} = \frac{nRT}{P}$$

$$= \frac{2.0(\text{mol}) \times 0.083(\text{bar L K}^{-1}\text{ mol}^{-1}) \times 300(\text{K})}{5 \times 10^6/10^5(\text{bar})}$$

$$= 1.004 \text{ L}$$

$$\text{Now, } Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{800 \text{ (mL)}}{1.004 \times 10^3 \text{ (mL)}} = 0.796$$

As Z is less than 1, it means that gas is more compressible under these conditions.

5. $V = 2$ L, $a = 3.648$ L bar K^{-1}

$T = 30$°C, $b = 0.0427$ L mol^{-1}

$m_{CO_2} = 154$ g

$$\therefore \text{Moles of } CO_2 = \frac{150}{44} \approx 3.41$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$\therefore P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} = 35.73 \text{ bar}$$

6. Yes, according to Charles' law, $V \propto T$.

7. No, temperature is lowered during adiabatic expansion.

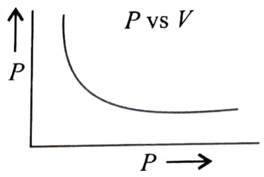
8. Pressure is exerted due to bombardment of gaseous molecules with the wall of container.

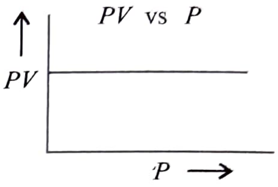
9. Rate of diffusion of H_2 is faster than that of air.

10. Gas pressure is due to bombardment of gas molecules against the walls of the container.

11. Barometer is an instrument to measure atmospheric pressure whereas manometer measures gas pressure.

12.





13. It cuts the volume axis at 0°C but it cuts the temperature axis at –273.15°C, i.e., absolute zero.

14. According to Charles' law, $V \propto (t + 273)$ at constant P and n.

15. $PV = \frac{m}{Mw}RT$

or $V = \frac{mRT}{MwP}$, where Mw = molar mass or molecular weight

16. If the collisions are non-elastic, there would be constant loss of energy. This would cause molecular motion to slow down and ultimately settle down at the bottom of the container like precipitate.

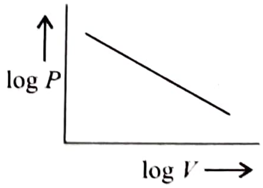
17. (1) Volume of a gas molecule is negligible in comparison to the total volume of container.

    (2) There is no force of attraction between the gaseous molecules.

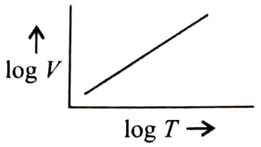
18. $\mu_{\text{most probable}} : \mu_{\text{av}} : \mu_{\text{rms}} = 1:1.128:1.224$

19. This implies that at this value of pressure, attractive and repulsive forces balance each other. Below this pressure attraction dominates and $Z < 1$. Above this pressure, repulsion dominate and $Z > 1$.

20. Plot of log P vs log V



21. Plot of log V vs log T



22. No, because gases condense to liquids and solids before this temperature is reached.

23. KE $\propto \sqrt{T}$

So ratio of $V = 1:1$

24. Dispersion forces are the attractive forces among non-polar molecules such as H_2, He, etc., while dipole–dipole forces are attractive forces among the polar molecules.

25. Because of surface tension, the molecules tend to minimise the surface area, and sphere has minimum surface area.

26. If a liquid is heated to the critical temperature of its vapour, the vapour pressure of liquid becomes equal to the vapour pressure of its vapour.

27. A gas with $a = 0$ means absence of intermolecular forces. Hence, such a gas cannot be liquified.

Exercises

Single Correct Answer Type

1. **(1)** Melting point of ice = 273 K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{1000}{273} = \frac{400}{T_2} \text{ (at constant } V)$$

$$T_2 = 109.2$$

2. **(4)** $\dfrac{F-32}{180} = \dfrac{C}{100}$

$$t - 32 = \frac{9t}{5}$$

$$t = -40°$$

3. **(2)** $PV = nRT = \dfrac{w}{m}RT$

$$P = \frac{dRT}{m}$$

$$d \propto \frac{P}{T}$$

$$\frac{d_{(\text{top})}}{d_{(\text{bottom})}} = \frac{710}{273} \times \frac{303}{760} = 1.04:1$$

4. **(1)** Effective pressure = 750 – 100 = 650 torr

Use $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

5. **(1)**

(1) 22.4 L N_2 gas at STP = 1 mol N_2

$= N_0$ molecules of N_2

$= 2N_0$ atoms of N

(2) $\dfrac{500 \times 2}{1000} = 1$ mol of NH_3

$= N_0$ molecules of NH_3

$= N_0$ atoms of N

(3) 1 mol of $NH_4Cl = N_0$ atoms of N

(4) 6.02×10^{23} NO_2 molecules $= 6.02 \times 10^{23}$ atoms of N

6. **(4)** $4.8 \text{ g } O_2 = \dfrac{4.8}{32} \text{ mol } O_2 = \dfrac{4.8}{32} \times 2 \text{ g } H_2 = 0.3 \text{ g}$

7. **(1)** $\left[P + \dfrac{a}{V^2}\right]V = RT$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$\frac{PV}{RT} = Z \text{ (compressibility factor)}$$

$$= \left(1 - \frac{a}{RTV}\right)$$

8. **(2)** $\text{KE} = \dfrac{3}{2}RT$

$$PV = RT = \frac{2}{3}(\text{KE})$$

9. **(3)** $PV = RT$ if $P_1 > P_2$, $V_1 < V_2$.

Also $\log P = -\log V + \log RT$

10. **(3)** Draw a line at constant P parallel to volume axis. Take volume corresponding to each temperature.

From volume axis, $V_1 > V_2 > V_3$

Hence, $T_1 > T_2 > T_3$.

11. **(3)** $P_1V_1 = n_1RT_1$

$$P_2V_2 = n_2RT_2$$

$$\frac{P_2V_2}{P_1V_1} = \frac{n_2T_2}{n_1T_1}$$

$$\frac{P_1}{9P_1}\frac{V_2}{30} = \frac{1}{2}\frac{n_1}{n_1}\frac{3T_1}{T_1}$$

$$V_2 = 405 \text{ mL}$$

12. **(1)** $PV = nRT$

$$n_1T_1 = n_2T_2$$

$$n_2 = \frac{T_1}{T_2} = \frac{3}{4}$$

13. **(2)** $P = \dfrac{n}{V}RT = \dfrac{w}{mV} = RT$

$$P = \frac{dRT}{m}$$

$$d \propto \frac{P}{T}$$

14. **(1)** $(f_1)^X = \dfrac{n'_{SO_2}}{n'_{O_2}} \times \dfrac{n_{O_2}}{n_{SO_2}}$, where n_{SO_2} and n_{O_2} are moles present initially.

$$\text{or } X \log f_1 = \log\left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}}\right]$$

$$\therefore X \log \sqrt{\frac{M_{O_2}}{M_{SO_2}}} = \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}} \right]$$

$$X \log \sqrt{\frac{32}{64}} = \log \frac{1}{1} \times \frac{1}{16}$$

$$\therefore X = 8;\ \text{also}\ \frac{n_1}{n_2} = \frac{r_1}{r_2} = \sqrt{\frac{32}{64}} = 0.707$$

$$\text{If } X = 6, \text{ then } 6 \log \sqrt{\frac{32}{64}} = \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}} \right]$$

$$= \log \left[\frac{n'_{SO_2}}{n'_{O_2}} \times \frac{1}{16} \right]$$

$$\frac{n'_{SO_2}}{n'_{O_2}} = 2:1$$

Rate of diffusion is $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$, i.e., 0.707 in each operation.

15. **(3)** $PV = nRT$ or $\log V = \log T + \log \frac{nR}{P}$

Slope = $\tan\theta = \tan 45° = 1$

$$\text{Intercept} = \log \frac{nR}{P} = \log \left[\frac{2 \times 0.0821}{0.0821} \right] = 0.3010$$

16. **(4)** $P(V - b) = RT$

$$d = \frac{R}{(V-b)} . T \Rightarrow \text{slope} = \frac{R}{V-b}$$

$$PV - Pb = RT$$

$$V = \frac{RT}{P} + b \quad \text{slope} = \frac{R}{P} \text{ and intercept } b$$

$$V = \frac{PV}{RT} = 1 + \frac{Pb}{RT}; Z > 1$$

i.e., repulsive forces predominate.

17. **(2)**

18. **(3)** 1 mol of O_2 = 1 mol SO_2

32 g O_2 = 64 g SO_2

19. **(1)** $KE = \frac{3}{2} RT$

$KE \propto T$

20. **(3)**

$Z = \frac{P_C V_C}{RT_C} = \frac{3}{8}$; each molecule moves with altogether different speed.

21. **(4)**

22. **(2)** Point A represents the most probable distribution of molecules. Hence, the most probable velocity is $\sqrt{2RT/M}$.

23. **(3)** Use $PV = RT$

24. **(3)** For real behaviour, $\frac{PV}{RT} \neq 1$.

25. **(4)** For n mol of a real gas

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

When volume of molecules can't be neglected,

$$P(V - nb) = nRT$$

$$PV = nRT + nbP$$

26. **(3)** As P increases, PV also increases, hence graph II.

27. **(1)** From Q. 25, when $\frac{n^2 a}{V^2} \neq 0$

$$\left(P + \frac{n^2 a}{V^2} \right) V = nRT$$

$$PV + \frac{n^2 a}{V} = nRT$$

$$PV = nRT - \frac{n^2 a}{V}$$

28. **(3)** $\chi_M = \frac{n_1}{h_T}$ $\left[\begin{array}{l} n_1 = \text{moles of one gas} \\ n_T = \text{Total no. of mixture of gases} \end{array} \right]$

$\chi_P = \frac{P_1}{P_T}$ $\left[\begin{array}{l} P_1 = \text{Pressure of one gas,} \\ P_T = \text{Total pressure of mixture of gases} \end{array} \right]$

$\chi_V = \frac{V_1}{V_T}$ $\left[\begin{array}{l} V_1 = \text{Volume of one gas} \\ V_T = \text{Total volume of mixture of gases} \end{array} \right]$

According to gas equation,

$P_1 V_1 = n_1 R_T$ ...(i) and $P_T V_T = n_T R_T$ ...(ii)

From Eqs. (i) and (ii)

$n_1 = \frac{P_1 V_1}{RT}$ ...(iii) $n_T = \frac{P_T V_T}{RT}$ ...(iv)

Divide Eq. (iii) by Eq. (iv),

$$\frac{n_1}{n_T} = \chi_M = \frac{P_1 V_1 \times \cancel{RT}}{\cancel{RT} \times P_T V_T} = \frac{P_1}{P_T} \times \frac{V_1}{V_T} = \chi_P \times \chi_V$$

$$\therefore \chi_M = \chi_P \times \chi_V$$

29. **(4)** $\bar{u} = \sqrt{\frac{8RT}{\pi m}}$

$$\bar{u} \propto \sqrt{\frac{T}{M}}$$

(1) $\bar{u} \propto \sqrt{\frac{560}{28}} = \sqrt{20}$

(2) $\bar{u} \propto \sqrt{\frac{500}{20}} = \sqrt{25}$

(3) $\bar{u} \propto \sqrt{\frac{440}{44}} = \sqrt{11}$

(4) $\bar{u} \propto \sqrt{\frac{140}{4}} = \sqrt{35}$

30. **(3)** $P_1 V_1 = n_1 RT_1$

$$P_2V_2 = n_2RT_2$$

$$\frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{300}{400} = \frac{3}{4}$$

$$n_2 = \frac{3}{4}n_1$$

$$\text{Escaped} = \frac{1}{4}$$

31. **(1)** $PV = RT$ for ideal gases.

32. **(2)** H_2 gas is greater than diffuses into balloon because rate of diffusion of H_2 is greater than the rate of diffusion of ethyne. Hence, it is enlarged.

33. **(2)** $P_1V_1 = n_1RT_1$

$$P_2V_2 = n_2RT_2$$

$$\frac{n_2}{n_1} = \frac{P_2}{P_1}$$

$$n_2 = 0.1 \times \frac{0.01}{100} = 10^{-5}\ \text{mol} = 6 \times 10^{18}\ \text{molecules}$$

34. **(2)**

35. **(3)** Gases which can be liquefied easily have high value of a and low value of b. So the answer is (c).

36. **(1)** $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

At low pressure, volume is high and b may be ignored. So van der Waals equation becomes

$$\left(P + \frac{a}{V^2}\right)V = RT$$

Hence, the answer is (a).

37. **(4)** b is equal to 4 times the volume of molecules in one mole of a gas (N_0 molecules)

Volume of one molecule = v

Volume of N_0 molecule = vN_0

Hence, $b = 4v\,N_0$

38. **(2)** Mean free path is the average distance travelled by a particle between two collisions.

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N}$$

where σ is collision, N is the number of molecules per unit volume.

So, λ will be the highest for small value of σ.

H_2 will have small σ.

Hence, the answer is (2).

39. **(1)** $Z = \frac{PV}{nRT} = 0.5$

Now, $\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$

$\left[P + \frac{n^2a}{V^2}\right][V] = nRT$ (b is negligible)

$$PV^2 - nRTV + n^2a = 0$$

$$\therefore V = \frac{nRT \pm \sqrt{n^2R^2T^2 - 4n^2a \times b}}{2P}$$

Since, V is constant at given P and T, thus, discriminant is 0.

$$\therefore n^2R^2T^2 = 4n^2aP \text{ or } a = \frac{R^2T^2}{4P}$$

$$= \frac{(0.0821)^2 \times (273)^2}{4 \times 100}$$

$$= 1.256\ \text{L mol}^{-2}\ \text{atm}$$

40. **(4)**

41. **(1)** $\left[P + \frac{a}{V^2}\right][V - b] = RT$

$$\therefore \left[P + \frac{a}{V^2}\right]V = RT$$

or $V^2P - RTV + a = 0$

$$V = \frac{+RT \pm \sqrt{R^2T^2 - 4Pa}}{2P}$$

Since, V is constant at given P and T, V can have only one value or discriminant = 0

$$\therefore R^2T^2 = 4Pa \text{ or } a = \frac{R^2T^2}{4P}$$

$$= \frac{(0.821)^2 \times (273)^2}{4 \times 34.98}$$

$$= 3.59\ \text{dm}^6\ \text{atm mol}^{-2}$$

42. **(2)** $PV = \frac{w}{m}RT$ (for vapours of H_2O)

$P = 3.6 \times 10^3$ Pa; $V = 2 \times 10^{-3}$ m^3; $T = 300$ K

$$\therefore w_{H_2O} = \frac{3.6 \times 10^3 \times 18 \times 2 \times 10^{-3}}{8.314 \times 300 = 0.052}$$

$w_{H_2O} = 52$ g

Since, relative humidity = 60%, therefore, amount of H_2O = 52 × 0.6 = 31.2 g

43. **(4)** Molar ratio of N_2 and CO is 3 : 2, i.e., 300 bar and 200 bar, respectively.

$$\frac{n_{N_2}}{n_{CO}} = \sqrt{\frac{m_{CO}}{mN_2}} \times \frac{P_{N_2}}{P_{CO}} = \frac{300}{200} = \frac{3}{2}$$

44. **(2)** $Z = \frac{PV}{nRT} \Rightarrow n = \frac{PV}{nRT} = \frac{1 \times 1}{1.2 \times 0.0821 \times 273} = 0.037$

$\therefore$ Number of molecules = 0.037 × 6.023 × 10^{23}

$= 2.23 \times 10^{22}$

45. **(1)** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $\left[\begin{matrix} V_1 = \text{inital} \\ V_2 = \text{final volume} \end{matrix}\right]$

$$\frac{PV_1}{T} = \frac{P}{4} \times \frac{V_2}{2T} \Rightarrow V_1 = \frac{V_2}{8} \Rightarrow V_2 = 8V_1$$

46. **(2)** On increasing the temperature, mobility of the molecules increases or vapourisation increases. Thus, the surface tension decreases.

47. **(4)**

48. **(3)** $\mu_{rms}(H_2) = \sqrt{\frac{T}{M}} = \sqrt{\frac{50}{2}} = 5$

μ_{rms} of $O_2 \propto \sqrt{\frac{T}{M}} = \sqrt{\frac{800}{32}} = 5$

Therefore, the ratio is 1.

49. **(1)** C_{P1} for 'He' $= \frac{5}{2}R : C_{P_2}$ *for* $H_2 = \frac{7}{2}R$

$n_{He} = 2; n_{H_2} = 1$

$$C_p = \frac{n_1 C_{P_1} + n_2 C_{P_1}}{n_1 + n_2} = \frac{2 \times \frac{5}{2}R + 1 \times \frac{7}{2}R}{3}$$

$$= \frac{17R}{6}$$

50. **(2)** Capillary rise decreases with increase in the radius of tube.

51. **(2)** Depression in the surface takes place when intermolecular attraction force of liquid called cohesive force dominates the force of attraction between the liquid and the capillary called adhesive force.

52. **(3)**

53. **(3)**

54. **(2)**

55. **(1)** $PV = nRT$

$$n = \frac{PV}{RT}$$

Number of molecules $= N_A \frac{PV}{RT}$

$$= \frac{PV}{(R/N_A)T} = \frac{PV}{K_B T}$$

where K_B = Boltzman constant

56. **(3)** $PV = \frac{M}{m}RT$

$$P \times 1 = \frac{M_{N_2}}{28}RT$$

$$P \times \frac{7}{8} = \frac{M_{O_2}}{32}RT$$

Dividing Eq. (i) by Eq. (ii), we get

$M_{N_2} = M_{O_2}$

57. **(1)** $V_{ideal} = 22.4$ L

$$\therefore PV_{ideal} = \frac{5.6}{22.4}RT = 0.25RT$$

58. **(1)** According to Boyle's law, $V \propto \frac{1}{P}$ at constant T.

59. **(1)** $Pm = dRT$

$$\frac{P_A m_B}{P_B m_B} = \frac{d_A RT}{d_B RT}$$

$$\frac{P_A}{B_B} \times \frac{1}{3} = 2$$

$P_A : P_B = 6 : 1$

60. **(3)** Charles' law $V \propto T$

61. **(1)** Given

$V_1 = 100$ mL

$P_1 = 10.4$ Pa

$V_2 = ?$

$P_2 = 105$ Pa

$P_1V_1 = P_2V_2$

$$\therefore V_2 = \frac{P_1V_1}{P_2} = \frac{105 \times 100}{10.4} = 10 \text{ mL}$$

62. **(3)** $V_1 = 100$ mL, $T_1 = 27°C = 300$ K

$P_1 = 740$

$V_2 = 80$ mL

$T_2 = ?$

$P_2 = 740$ mm

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\therefore T_2 = \frac{V_2 \times T_1}{V_1} = \frac{80 \times 300}{100} = 240 \text{ K}$$

or $T_2 = -33°C$

63. **(1)** $P_1 = 730$ mm

$V_1 = 730$ mL

$V_2 = ?$

$P_2 = 760$ mm

$\therefore P_1V_1 = P_2V_2$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{730 \times 730}{760} = 701 \text{ mL}$$

64. **(3)** $(d)_1 = d$

$(d)_2 = 0.75\ d$

$P_1 = 1$ atm; $T_1 = 27°C = 300$ K

$P_2 = 1$ atm; $T_2 = ?$

$$\left(\frac{d_1}{d_2}\right) = \frac{P_1 \times T_2}{T_1 \times P_2} \text{ or } \frac{T_2}{T_1}$$

$$\therefore T_2 = \frac{d_1}{d_2} \times T_1 = \frac{d}{0.75\ d} \times 300 = 400 \text{ K}$$

65. **(4)** KE $= \frac{3}{2}RT$ or $\frac{3}{2}PV$

66. **(1)** $\mu_{rms} = \sqrt{\frac{3\ RT}{Mw}}$ or $\mu_{rms} \propto \sqrt{\frac{1}{Mw}}$

Hence, He > N_2 > O_2 > HBr

67. **(4)**

68. **(1)** Rate of diffusion $\propto \sqrt{\frac{1}{Mw}}$

$$\therefore \frac{\frac{1}{t_{O_2}}}{\frac{1}{t_{N_2}}} = \sqrt{\frac{M_{N_2}}{M_{O_2}}} = \sqrt{\frac{2.8}{3.2}} = 0.93$$

or $\frac{t_{N_2}}{t_{O_2}} = 0.93$

$\therefore t_{N_2} = 0.93 \times 10 = 9.3$ min

69. **(4)** $KE = \frac{3}{2}nRT$

$n = 1$, for molar kinetic energy

$$\left(\frac{3}{2}\times 1\times R\times T\right)_{\text{Helium}} = \left(\frac{3}{2}\times 1\times R\times 400\right)_{\text{Argon}}$$

$T = 400$ K

70. **(3)** Gases and liquid do not possess definite volume.

71. **(2)** Thermal energy >> Molecular attraction

72. **(3)**

73. **(2)** b(co-volume) $= 4\left(\frac{4}{3}\pi r^3\right)$

$= 4$(Volume occupied by gaseous molecule)

74. **(4)** $KE = \frac{3}{2}RT$

or $KE \propto T$

75. **(4)** $PV = nRT$

$$PV = \frac{w}{m}RT$$

$$P_{O_2}V = \frac{w}{32}RT \qquad \text{...(i)}$$

$$P_{O_2}V = \frac{w}{28}RT \qquad \text{...(ii)}$$

$$\frac{P_{O_2}}{P_{N_2}} = \frac{28}{32}$$

$P_{O_2} = 0.875\, P_{N_2}$

76. **(2)** $PV = nRT$

n moles of the gas have a volume V.

77. **(2)** At low temperature and high pressure, gases deviate more from ideal condition.

78. **(4)** Ideal gas has no force of attraction and has negligible volume. Hence, it cannot be liquefied at any T and P.

79. **(1)** $KE_{CO} = KE_{N_2}$

Because $KE = \frac{3}{2}RT$. It only depends upon temperature.

80. **(3)** $\mu_{av} = \sqrt{\frac{8RT}{\pi M}}$

81. **(2)** $\mu_{rms} = \sqrt{\frac{3\,RT}{M}}$

$M_{CO_2} = 44$ g

$M_{C_3H_8} = 44$ g

$\therefore (\mu_{rms})_{CO_2} = (\mu_{rms})_{C_3H_8}$

82. **(4)** $V_1 = 15$

$P_1 = 1$ atm

$T_1 = 0°C$ or 273.15 K

$P_2 = 2$ atm

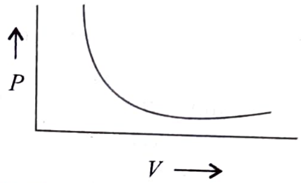
$T_2 = 273°C$ or 546.15 K

$V_2 = ?$

$$\therefore V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} = \frac{1\times 15}{273.15} \times \frac{546.15}{2} = 15\text{ L}$$

83. **(3)**

84. **(3)**



Boyle's law

$PV = K$ (constant)

85. **(2)** **86.** **(2)**

Multiple Correct Answers Type

1. **(1, 2, 3, 4)** Refer Section 5.13.1.

2. **(1, 4)**

Hint: Average speed $\mu_{av} = \sqrt{\frac{8RT}{\pi M}}$

$\therefore \mu_{av} \propto \frac{T}{M}$

3. **(2, 4)**

Hint: Average speed $\mu_{av} \propto T$

4. **(3, 4)**

5. **(1, 4)**

Hint: $\mu_{av} = \sqrt{\frac{8RT}{\pi M}}$ and $\mu_{rms} = \sqrt{\frac{3RT}{M}}$

6. **(1, 3, 4)**

Hint: $\frac{\mu_{av}}{\mu_{rms}} = \sqrt{\frac{8RT}{\pi M}} \Big/ \sqrt{\frac{3RT}{M}} = \sqrt{\frac{8}{\pi 3}}$

Hence, the ratio of μ_{av} and μ_{rms} is independent of temperature.

$KE_{av} = \frac{3}{2}RT$ (hence, it is independent of mean speed)

7. **(1, 4)**

Hint: When $\frac{T_A}{M_A} = \frac{T_B}{M_B}$ or $T_AM_B = T_BM_A$

$(PV)_A = nRT$ or $\frac{W_A}{M_A}RT_A$

and $(PV)_B = \frac{W_B}{M_B} RT_B$

∴ When $W_A = W_B$

$(PV)_A = (PV)_B$

$$\mu_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$\therefore \mu_A = \sqrt{\frac{3RT_B}{M_A}}$$

$$\mu_B = \sqrt{\frac{3RT_B}{M_B}}$$

$$\therefore \mu_A = \mu_B \qquad \left(\frac{T_A}{M_A} = \frac{T_B}{M_B}\right)$$

8. (1, 2, 4)

Hint: At critical point, the gases can be liquefied and hence there is force of attraction.

At high pressure and low temperature, gases are close to each other and hence they experience force of attraction.

9. (3, 4)

Hint: Given,

$T_1 = 273°$ or 546.15 K

$P_1 = 1$ atm

$T_2 = 0°C$ or 273.15 K

$P_2 = ?$

$$\therefore \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\therefore P_2 = \frac{P_1 \times T_2}{T_1} = \frac{1 \times 273.15}{546.15}$$

$$= \frac{1}{273.1} \text{ atm or } 5.05 \times 10^4 \text{ N m}^{-2}$$

10. (1, 4)

$Z_{\text{real gas}} > 1$

∴ $V_m > 22.4$ L (Because $V_{\text{ideal}} = 22.4$ L)

Hence, when volume is higher, the gases are far apart and, therefore, difficult to liquefy.

11. (1, 2, 3)

12. (1, 3)

13. (2, 3)

Hint: Helium gas has lower molecular mass and hence it moves faster than neon and strikes the wall more frequently.

$$\mu_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}$$

$$\mu_{\text{av}} \propto \left(\frac{1}{M}\right)^{1/2}$$

Hence, He has higher speed than neon.

14. (1, 4)

Hint: $r \propto \frac{1}{\sqrt{M}}$

$$\therefore \frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{16}{1}} = 4$$

$\therefore r_{H_2} = 4 \times r_{O_2}$

$\left(\frac{\partial T}{\partial P}\right)_H = 0$ (for ideal gas)

Because $T \propto P$ (for ideal gas)

$\therefore \frac{T}{P} = K$ (constant)

15. (2, 3)

Hint: $\mu_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ or $\sqrt{\frac{3PV}{M}}$

$(\mu_{\text{rms}})_1 = 5 \times 10^4$ cm s^{-1}

$(\mu_{\text{rms}})_2 = 10 \times 10^4$ cm s^{-1}

$$\therefore P_1 = \frac{(\mu_{\text{rms}})_1^2 \times M}{3V} = (5 \times 10^4)^2 \times \frac{M}{3V}$$

$$P_2 = \frac{(\mu_{\text{rms}})_2^2 \times M}{3V} = (10 \times 10^4)^2 \times \frac{M}{3V}$$

$$\text{or } \frac{P_2}{P_1} = \frac{(10 \times 10^4)^2}{(5 \times 10^4)^2} = \frac{100}{25} = 4$$

$\therefore P_2 = 4 \times P_1$

Similarly, $T_2 = 4 \times T_1$

16. (1, 2, 3)

R (gas constant) depends only upon the units of measurement.

17. (1, 2, 4)

18. (2, 4) Boyle's law $P \propto \frac{1}{V}$ ∴ $\left(\frac{\partial P}{\partial V}\right)_T = -K/V^2$

19. (2, 4) Dipole and van der Waals force

20. (1, 4) Charles' law, $V \propto T$ ∴ $\left(\frac{\partial V}{\partial T}\right)_P = K$

21. (3, 4) Volume and pressure of gas

22. (1, 2) Charles' law, $V \propto T$

23. (2, 4)

24. (1) SO_2 gas

25. (1, 3) $R = \frac{PV}{nT}$ ∴ R (unit) = L atm K^{-1} mol^{-1} and atm cm^3 K^{-1} mol^{-1}

26. (2, 3) Because molecular mass is almost same

27. (1, 3) Real gases have volume and force of attraction.

28. (1, 3) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$, at high pressure

$$P >> \frac{an^2}{V^2}$$

29. (2, 3) These gas mixtures react with each other.

30. (1, 2, 3)

31. (1, 2, 3, 4)

Linked Comprehension Type

1. (1) Let n_A be the amount of H_2 and n_B be the amount the CH_4.

We know that

$$n_A = \frac{m}{2}; n_B = \frac{m}{16}$$

where m is the mass of the gas of two flasks A and B

$$\therefore \frac{n_A}{n_B} = \frac{m}{2} \Big/ \frac{m}{16} = 8$$

Now, the number of molecules in these flasks are given as

$$N_A = \frac{m}{2} \cdot N, N_B = \frac{m}{16} N,$$

where N is Avogadro's constant.

$$\therefore \frac{N_A}{N_B} = 8$$

$$\Rightarrow N_A > N_B$$

2. (1) Since $P_A V = n_A R T_A$ and $P_B V = n_B R T_B$

$$\therefore \frac{P_A}{P_B} = \frac{n_A T_A}{n_B T_B} = 8 \times \frac{300}{600} = 4$$

$$\therefore P_A > P_B \text{ or } P_A = 4P_B$$

3. (3) Both the gases will have same compressibility factor, i.e., 1, since both of them are ideal gases.

4. (1) Since total KE = KE × Number of molecule

$$\therefore \text{Total (KE)}_A = \frac{3}{2} k T_A N_A$$

$$\text{Total (KE)}_B = \frac{3}{2} k T_B N_B$$

Hence

$$\frac{\text{Total (KE)}_A}{\text{Total (KE)}_B} = \frac{T_A N_A}{T_B N_A} = \frac{300}{600} \times 8 = 4$$

$$\therefore \text{Total (KE)}_A > \text{Total (KE)}_B$$

5. (2) Since KE per mole $= \frac{3}{2} RT$,

$$\text{KE per mole of } A = \frac{3}{2} R T_A$$

$$\text{KE per mole of } B = \frac{3}{2} R T_B$$

Hence

$$\frac{\text{KE per mol of } A}{\text{KE per mol of } B} = \frac{T_A}{T_B} = \frac{300}{600} = \frac{1}{2}$$

$$\therefore \text{KE per mol of } A < \text{KE per mol of } B$$

6. (1) Since $(\mu_{av})_A = \sqrt{\frac{8RT_A}{\pi M_A}}$

$$(\mu_{av})_B = \sqrt{\frac{8RT_B}{\pi M_B}}$$

Hence

$$\frac{(\mu_{av})_A}{(\mu_{av})_B} = \sqrt{\frac{T_A}{M_A}} \times \sqrt{\frac{M_B}{T_B}} = \sqrt{\frac{300}{2}} \times \frac{16}{600} = 2$$

$$\therefore (\mu_{av})_A > (\mu_{av})_B$$

7. (2) Since $T_c = \frac{8a}{27Rb}$

Hint: Gas B has the highest value of a, therefore, it has the highest critical temperature.

8. (3) Since molecular volume $V = 3b$

For gas $A = V_A = 3 \times 0.027 = 0.069 \text{ dm}^3$

For gas $B = V_B = 3 \times 0.030 = 0.090 \text{ dm}^3$

For gas $C = V_C = 3 \times 0.032 = 0.096 \text{ dm}^3$

$\therefore V_C > V_B > V_A$

9. (1) At STP the compressibility factor for gas A

10. (4) The units of measurement.

11. (4) The product of P and V always remains constant (Boyle's law).

12. (1) The ideal gas equation is

$$PV = nRT$$

$$\text{or } P = \frac{\rho RT}{M}, \text{ or } PV = RT\ (n = 1)$$

13. (2) $\rho = \frac{PM}{RT}$

14. (3) $P \propto \frac{1}{V}$

15. (2) Real gas

16. (3) $\left(P + \frac{a}{V^2}\right)$

17. (2) $V - b$

18. (1) At high pressure $V >> b$.

$$\text{Hence, } \left(P + \frac{a}{V^2}\right) V = RT$$

19. (2) $Z = \frac{PV}{RT}$ $\quad \therefore Z_{ideal} = 1$

20. (4) $Z_{real} \neq 1$

21. (2) Volume of a real gas at $Z_{real} < 1$ will be < 22.4 L

22. (1) $Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}$

Matrix Match Type

1. **(a → q; b → p; c → r)**
2. **(a → r; b → p; c → s; d → q)**
3. **(a → s; b → r; c → q; d → p)**
4. **(a → t; b → p; c → q; d → r; e → s)**
5. **(a → q; b → s; c → t; d → p; e → r)**
6. **(a → p; b → r; c → q; d → s)**
7. **(a → p; b → q; c → r; d → s)**

   (a → p) because diffusion r proportion to $\sqrt{1/M}$. Therefore, low molar mass has high rate of diffusion.
8. **(a → r)**

$Z = \dfrac{PV}{RT}$; for ideal gas $Z = 1$

(b → s)

van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

For 1 mol gas,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, gas equation becomes

$P(V - b) = RT$

$PV - Pb = RT$

or $PV = RT + Pb$

Dividing by RT, we get

$$\frac{PV}{RT} = \frac{RT}{RT} + \frac{Pb}{RT}$$

or $Z = 1 + \dfrac{Pb}{RT}$

(c → q)

van der Waals equation for 1 mol gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At high pressure, $b << V$; hence, equation becomes

$$\left(P + \frac{a}{V^2}\right)V = RT$$

or $PV + \dfrac{a}{V} = RT$

or $PV = RT - \dfrac{a}{V}$

Dividing by RT, we get

$$\frac{PV}{RT} = \frac{RT}{RT} - \frac{a}{VRT}$$

or $Z = 1 - \dfrac{a}{VRT}$

(d → p)

$$Z = \frac{P_cV_c}{RT_c} = \frac{3}{8}$$

9. **(a → q; b → r; c → s; d → p)**

Attractive forces: $Z < 1$; in high-pressure region, $Z > 1$.

At critical points $Z = 3/8$ for gas at low pressure and very high temperature Z . 1.

10. **(a → s; b → t; c → r; d → q; e → p)**

Numerical Value Type

1. **(2)** Inversion temperature $(T_i) = \dfrac{2a}{Rb}$

Boyle's temperature $(T_b) = \dfrac{a}{Rb}$

$\therefore \dfrac{T_i}{T_b} = 2$

2. **(1)** $T_i = 350$ K; $T_f = 700$ K

KE_{avg} (Translational) $= \dfrac{3}{2}$ KT

$\therefore$ KE increase by a factor of $\dfrac{700}{350} = 2$

3. **(2)** $Z_{\text{(ideal gas)}} = \dfrac{V_m}{V_{\text{ideal}}} = 1$

4. **(4)** $b = 4$(volume of gas molecule)

$$\therefore \frac{b}{\text{Volume of gas molecule}} = 4$$

5. **(2)** Rate of diffusion $= \sqrt{\dfrac{1}{\text{Molecular mass}}}$

$$\therefore \frac{r_A}{r_B} = \sqrt{\frac{44}{11}} = \sqrt{4} = 2$$

6. **(3)** Given $V_1 = 1$ L; $T_1 = 100$ K; $T_2 = 300$ K; $V_2 = ?$

We know, $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2} \Rightarrow V_2 = \dfrac{V_1T_2}{T_1}$

$$\therefore V_2 = \frac{1 \times 300}{100} = 3$$

7. **(2)** $u_{\text{av}} = \sqrt{\dfrac{8RT}{\pi M}}$, $T = 100$ K; $M = 529.5$ g mol^{-1}

$$= \sqrt{\frac{8 \times 8.314 \times 100}{3.14 \times 529.5}} = 2$$

$\therefore$ Average speed of molecule is 2 or (b)

8. **(4)** $PV = nRT$; $n = \dfrac{RT}{PV} = \dfrac{0.082 \times 97.5}{2 \times 1} = \dfrac{8}{2} = 4$

9. **(3)** Given, $P = 1.56$ atm; $V = 10$ L

$T = 317$ K; $R = 0.082$

Total moles $(n) = \dfrac{PV}{RT} = \dfrac{1.56 \times 10}{0.082 \times 317} = 0.6$ mol

Let CxH_8 be a mol, therefore moles of $C_xH_{12} = (0.6 - a)$ mol; mass of C in a mol of $C_xH_{12} = 12ax$ g; mass of C in $(0.6 - a)$ mol of $C_xH_{12} = 12 \times (0.6 - a)$ g

$\therefore$ Total mass of C in mixture $= 12ax + 12x(0.6 - a)$g

$= 41.4$ g

% of C in mixture $= \dfrac{7.2x}{41.4} \times 100$

Given % of $C = 87\%$

or $\dfrac{720x}{41.4} = 87$ or $x = 5$

10. **(2)** $r_{CH_4} = 2r_X$, we know $r = \sqrt{\dfrac{1}{\text{Molecular mass}}}$

$$\therefore \frac{r_{CH_4}}{r_X} = \sqrt{\frac{M_X}{M_{CH_4}}} \Rightarrow \frac{2r_X}{r_X} = \sqrt{\frac{M_X}{16}}$$

or $M_X = 64$

Given Molecular mass is divided by 32 therefore,

$$X = \frac{M_X}{32} = \frac{64}{32} = 2$$

Archives

JEE Main

Single Correct Answer Type

1. (4) Number of moles,

$$n = \frac{pV}{RT} = \frac{3170 \times 10^{-3}}{8.134 \times 300} = 1.27 \times 10^{-3} \text{ mol}$$

2. (4) van der Waals' constants a is due to force of attraction and b due to finite size of molecules.

Thus, greater the value a and smaller the value of b, larger will be the liquefaction.

Thus, $a\,(Cl_2) > a\,(C_2H_6)$

And $b\,(Cl_2) < b\,(C_2H_6)$

3. (4) Molecular velocity can be

$$\text{Average velocity} = \frac{\sqrt{8RT}}{\pi M}$$

$$\text{Root mean square velocity} = \sqrt{\frac{3RT}{M}}$$

$$\text{Most probable velocity} = \sqrt{\frac{2RT}{M}}$$

In all cases, molecular velocity $\propto \sqrt{T}$

4. (2)

Rate of diffusion, $r \propto p$

$$r = \frac{1}{\sqrt{M}} \therefore r \propto \frac{p}{\sqrt{M}}$$

$$\text{For gas A, } r_A \propto \frac{p_A}{\sqrt{M_A}} \qquad (1)$$

$$\text{For gas B, } r_B \propto \frac{p_B}{\sqrt{M_B}} \qquad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{r_A}{r_B} = \frac{p_A}{p_B}\sqrt{\frac{M_B}{M_A}} \text{ or } \frac{p_A}{p_B}\left(\frac{M_B}{M_A}\right)^{1/2}$$

5. (3) van der Waals' equation for one mole of real gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

When pressure is high $p >> \frac{a}{V^2}$

Such that $\left(p + \frac{a}{V^2}\right) \approx p$

Thus, $p(V - b) = RT$

$pV - pb = RT$

$pV = RT + pb$

$\therefore$ Compressibility factor,

$$Z = \frac{pV}{RT} = \left(1 + \frac{pb}{RT}\right)$$

6. (3)

$C^* = \text{most probable speed} = \sqrt{\frac{2RT}{M}}$

$\bar{C} = \text{average speed} = \sqrt{\frac{8RT}{\pi M}}$

$C = \text{Means square speed corrected as rms} = \sqrt{\frac{3RT}{M}}$

$$\therefore \quad \overset{*}{C} < \bar{C} < C$$

Hence, $\overset{*}{C} : \bar{C} : C = 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225$

[**Note:** As no option corresponds to means square speed, it is understood as misprint. It should be root mean square speed.]

7. (2) van der Waals equation is given by

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, V decreases. Thus, $\frac{a}{V^2}$ increases.

However, V is still large enough is comparison to b hence b can be neglected. Thus, van der Waals' equation becomes

$$\left(p + \frac{a}{V^2}\right)V = RT$$

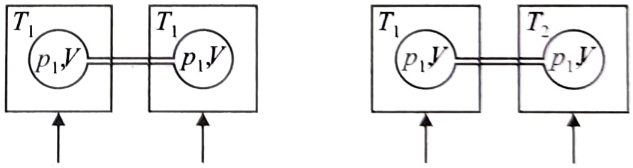
$$\Rightarrow \quad pV + \frac{a}{V} = RT$$

$$\Rightarrow \quad pV = RT - \frac{a}{V}$$

$$\Rightarrow \quad \frac{pV}{RT} = 1 - \frac{a}{RTV}$$

$$Z = 1 - \frac{a}{RTV} \qquad \left[\because \frac{pV}{RT} = Z\right]$$

8. (4)



$$n_1 = \frac{p_i V}{RT_1} \quad n_2 = \frac{p_i V}{RT_1} \quad n'_1 = \frac{p_f V}{RT_1} \quad n'_2 = \frac{p_f V}{RT_2}$$

$$n_1 + n_2 = n'_1 + n'_2$$

$$\frac{p_i V}{RT_1} + \frac{p_i V}{RT_1} = \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2}$$

$$\frac{2p_i V}{RT_1} = \frac{p_f V}{R}\left(\frac{T_1 + T_2}{T_1 T_2}\right)$$

$$p_f = \frac{2p_i T_2}{T_1 + T_2}$$

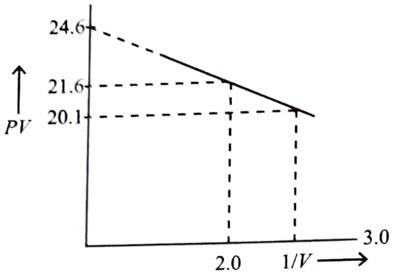
JEE Advanced

Single Correct Answer Type

1. (2) $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$

The term that is correct for the attractive forces present in a real gas in the van der Waals equation is an^2/V^2.

2. (3)



$$\left(P+\frac{a}{V^2}\right)(V)=RT$$

$$PV+a/V=RT$$

$$PV=RT-a/V$$

$$y=RT-a(X)$$

$$\text{So slope}=a=\frac{21.6-20.1}{3-2}=\frac{1.5}{1}=1.5$$

3. (3)

Multiple Correct Answers Type

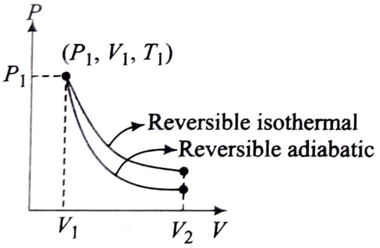
1. (1, 2, 3)

For free expansion

$W=0,\ q=0,\ T_2=T_1$ and $P_1V_1=P_2V_2$

2. (1, 3, 4)

(1)



Area under curve in reversible isothermal is more. So, more work will be done by gas.

(2) $T_1=T_2 \Rightarrow \Delta U=nC_V\Delta T=0$

In reversible adiabatic expansion, $T_2<T_1$

$\therefore\ \Delta T=-\text{ve}$

$\therefore\ \Delta U=-$ ve as $\Delta U=nC_V\Delta T$

(3) In Free expansion, $P_{\text{ext}}=0 \quad \therefore\ W=0$

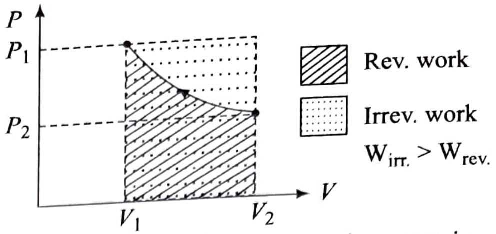
If carried out isothermally ($\Delta U=0$)

$\Rightarrow\ q=0$ (Adiabatic); From I law

If carried out adiabatically ($q=0$)

$\Rightarrow\ \Delta U=0$ (isothermal); From I law

(4)



During irreversible compression, maximum work is done on the gas (corresponding to shaded area)

3. (2, 3)

$\Delta H_{AC}+\Delta H_{CD}+\Delta H_{BA}=0$

$\Delta H_{BA}=0$ (Temperature is constant)

$\Delta H_{AC}=\Delta H_{BC}$ ...(1)

We know that $q_1=\Delta H$ (in path BC, $P=$ constant)

Hence $q_{BC}=\Delta H_{BC}$

From Eq. (1)

$q_{BC}=\Delta H_{AC}$

(2) $q_{BC}=-P(V_1-V_2)=P_2(V_2-V_1)$

(3) $\Delta H_{CA}=nC_P(T_1-T_2)=nC_P(T_2-T_1)$

$\Delta U_{CA}=nC_V(T_1-T_2)=-nC_V(T_2-T_1)$

As, $C_P>C_V$

So, $\Delta H_{CA}<\Delta U_{CA}$

Linked Comprehension Type

1. (3)

$XM_1=10, \qquad YM_2=40$

$$\frac{x}{24-x}=\sqrt{\frac{40}{10}} \Rightarrow \frac{x}{24-x}=\frac{2}{1}$$

$$x=48-2x$$

$$3x=48$$

$$x=\frac{48}{3}=16$$

2. (4) Larger the size of the molecules, smaller the mean free path.

$$\text{Collision frequency }(z)=\frac{\pi n^2\sigma^2\mu_{\text{av}}}{\sqrt{2}}\,(Z\propto\sigma^2)$$

$$\text{Mean free path }(\lambda)=\frac{1}{\sqrt{2}n\sigma^2}\left(\lambda\propto\frac{1}{\sigma^2}\right)$$

where, $n=$ No. of molecules per unit molar volume.

$\sigma=$ collision diameter.

Numerical Value Type

1. (4) $v_{\text{rms}}(X)=\sqrt{\frac{3RT}{M}}=\sqrt{\frac{3R\times 400}{40}}=\sqrt{30R}$

$$v_{\text{most probable}}(Y)=\sqrt{\frac{2RT}{M}}=\sqrt{\frac{2R\times 60}{M}}$$

Given $v_{\text{rms}}(X)=V_{\text{most probable}}(Y)$

$$\therefore \sqrt{30R} = \sqrt{\frac{2R \times 60}{M}}$$

or $M = 4$

2. **(4)**

Mean free path $(l) \propto \frac{T}{P}$

Mean speed $(C_{av}) \propto \sqrt{T}$

Diffusion coefficient (D) is proportional to both mean free path (l) and mean speed.

$$\therefore D \propto \frac{T^{3/2}}{P}$$

At temperature T_1 and P_1

$$D_1 = \frac{KT_1^{3/2}}{P_1} \quad \text{...(1)}$$

If T_1 is increased 4 times and P_1 is increased 2 times.

$$D_2 = \frac{K(4T_1)^{3/2}}{2P_1} \quad \text{...(2)}$$

$$\frac{D_2}{D_1} = \frac{(4)^{3/2}}{2} = \frac{2^3}{2} = 4$$

3. **(2.22)**

As in the fig 2, the system attains equilirbium, so,

PA = PB and TA = TB

$$\frac{P_A V_A}{Rn_A T_A} = \frac{P_B V_B}{n_B T_B R}$$

$$\frac{V_A}{V_B} = \frac{n_A}{n_B}$$

$$n_A = \frac{5}{400\,R}$$

$$n_B = \frac{3}{300\,R}$$

Due to sliding of piston vol. of A will be increased by x and that of B will be decreased by x.

$V_A = 1 + x$

$V_B = 3 - x$

$$\frac{1+x}{3-x} = \frac{\frac{5}{400\,R}}{\frac{3}{300\,R}}$$

$$4(1+x) = 5(3-x)$$

$$4x + 5x = 11 \Rightarrow x = \frac{11}{9}$$

Hence volume of container A will be

$$V_A = 1 + \frac{11}{9} = \frac{20}{9} = 2.22$$

Chapter 6

Concept Application Exercises

Exercise 6.1

1. $\Delta U = q + w = 25 - 15 = 10$ kJ

2. $\Delta U = q + w = -200 + 400 = 200$ J

3. $\Delta U = q + w$ or $460 = 710 + w \Rightarrow w = -250$ J

4. $\Delta U = q + w$ or $240 = q - 90$ or $q = 330$ kJ

Heat flows from surroundings to the system.

5. $w = -nRT \ln\frac{V_2}{V_1}$

$w = -(3) \times 8.314 \times 300 \times 2.303 \log 2$

$= -5187$ J

For isothermal process, $\Delta U = 0$

$\Delta U = q + w$

$0 = q - 5187 \Rightarrow q = 5187$ J

6. **a.** When heat is transferred to the surroundings, the total energy content of the system **decreases.** The system loses a part of energy in the form of heat.

b. When work is done on the system, the energy content of the system **increases.**

c. When work is done by the system, the energy content of the system **decreases.** The system does work at the cost of its energy.

7. Work done on the system,

$w = -p\,\Delta V = -(V_f - V_i)$

$p = 4$ atm, $V_i = \frac{nRT}{p}$

$n = 2$ mol $R = 0.082$ atm L mol^{-1} K^{-1},

$T = 273 + 27 = 300$ K, $p = 2$ atm

$V_i = \frac{2 \times 0.082 \times 300}{2} = 24.6$ L

and $V_f = \frac{V_i}{2} = \frac{24.6}{2} = 12.3$ L

$w = -4$ atm $\times (12.3 - 24.6)$ L

$= 49.2$ L-atm $= 49.2 \times 101.3$ J $= 4984$ J.

Since, it is isothermal compression, $\Delta U = 0$

Now, $\Delta U = q + w$

$0 = q + 4984$ J

or $q = -4984$ J

8. **(3)**

9. **(2, 3)** For cyclic process, $\Delta H = \Delta U = 0$

10. **(2)** $w = -n R\Delta T$ or $w = -p\,\Delta V = -1 \times 8.314 \times 1 = -8.314$ J

11. **(3)**

12. **(3)** $(T_1/3)^{0.4}$

13. **(1)** 3740 J

14. **(4)** $10.5RT_0$

Exercise 6.2

1. Work done by the system,

$w = P\,\Delta V = P(V_2 - V_1)$

$= 3.0(5 - 3) = 6$ L atm.

or $w = 6 \times 101.3$ J $= 607.8$ J ($\because$ 1 L atm $= 101.3$ J)

This work is used for heating water.

Molar heat capacity of water $= 4.184 \times 18$

$= 75.312$ JK^{-1} mol^{-1}

Now, $Q = mst$

$607.8 = 10 \times 75.312 \times t$ or $t = 0.81$ K

$\therefore$ Final temperature of water $= 290 + 0.81 = 290.81$ K.

2. Since, work is done against constant pressure and thus, irreversible.

Given, $\Delta V = (6 - 2) = 4$ L,

$P = 1$ atm

$W = -1 \times 4$ L-atm $= -\frac{1 \times 4 \times 1.987}{0.0821}$ cal

(Since 0.0821 L-atm = 1.987 cal)

$= -96.81$ cal $= -96.81 \times 4.184$ J ($\because$ 1 cal $= 4.184$ J)

$= -405.05$ J

Now, from the first law of thermodynamics

$q = \Delta U - W$

$800 = \Delta U + 405.05$

$\therefore \Delta U = 394.95$ J

3. Since the process is isothermal,

$\Delta U = \Delta H = 0$

From first law of thermodynamics,

$\Delta U = q + w = 0$

$q = -w$

$w = -2.303\,nRT \log\left(\frac{V_2}{V_1}\right)$

$= -2.303 \times 1 \times 8.314 \times 400 \log\frac{40}{20}$

$= -2.303 \times 1 \times 8.314 \times 400 \times 0.3010$

$= -2305.3$ J (work is done by the system)

$q = -w = 2305.3$ J (Heat is absorbed by the system)

4. From the first law of thermodynamics

$\Delta U = q + w$

$\Delta U = q + P\,\Delta U = 0 + \{-100\,(99 - 100)\}$

$= 100$ bar mL

$\Delta H = \Delta U + (P_2V_2 - P_1V_1) = 100 + (100 \times 99 - 1 \times 100)$

$= 9900$ bar mL

5. **(2)** $w = -2.303nRT \log\frac{V_2}{V_1}$

$= -2.303 \times 5 \times 8.314 \times 300 \log\frac{60}{6}$

$= -28.72$ kJ

6. (3) Initial volume, $V_1 = 10$ L

$$V_2(\text{final}) = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$$W = P\,\Delta V = 1 \times (249 - 10) = 239 \text{ L bar}$$

7. (1) $\Delta U = q + w = 20 - 10 = 10$ kJ

8. (1) **9. (2)** **10. (3)** **11. (1)**

12. (1) **13. (3)**

Exercise 6.3

1.

$$\begin{array}{ll}
Na(s) \longrightarrow Na(g) & \Delta H = ? \\
Na(g) \longrightarrow Na^{\oplus} + (g) + e^- & \Delta H_1 = 502.1 \\
\frac{1}{2}[Cl_2(g) \longrightarrow 2Cl(g)] & \Delta H_2 = 242.8 \times \frac{1}{2} \\
Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s) & \Delta H_3 = -411.1 \\
Na^{\oplus}(g) + Cl^{\ominus} \longrightarrow NaCl(s) & \Delta H_4 = -778.0 \\
Cl^{\ominus}(g) + e^- \longrightarrow Cl(g) & \Delta H_5 = -365.3
\end{array}$$

Rewriting:

$$\begin{array}{ll}
Na^{\oplus}(g) + e^- \longrightarrow NaCl(s) & \Delta H_1 = -502.1 \\
\frac{1}{2}[Cl_2(g) \longrightarrow 2Cl(g)] & \Delta H_2 = -\frac{242.8}{2} \\
Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(g) & \Delta H_3 = -411.1 \\
NaCl(g) \longrightarrow Na^{\oplus}(g) + Cl^{\ominus}(g) & \Delta H_4 = 778.0 \\
Cl^{\ominus}(g) \longrightarrow Cl(g) + e^- & \Delta H_5 = 365.3 \\
\hline
Na(s) \longrightarrow Na(g) & \\
\hline
\end{array}$$

or

$$\Delta H = -502.1 - \frac{242.8}{2} - 411.1 + 778 + 365.3$$

$$= -502.1 - 121.4 - 411.1 + 1143.3$$

$$= -1034.6 + 1143.3 = 108.7 \text{ kJ mol}^{-1}$$

2. Inhaled O_2 in one breath $= \frac{200 \times 20}{100}$ mL $= 40$ mL

Exhaled O_2 in one breath $= \frac{200 \times 10}{100}$ mL $= 20$ mL

Used O_2 in one breath $= 40 - 20 = 20$ mL

Now 20 breaths are taken in 1 min

Breath taken in 1 hour $= 20 \times 60 = 1200$ breath

Volume of O_2 used in 1 h

$= 20 \times 1200 = 24000$ mL at 27°C

$= \frac{24000}{300} \times 273$ mL at 0°C

$= 21840$ mL $= 21.84$ L at 0°C

For glucose:

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O \quad \Delta H = -2822.5$ kJ

6×22.4 L of O_2 is used for 180 g glucose

21.84 L of O_2 is used for $= \frac{180 \times 21.4}{6 \times 22.4} = 29.25$ g

Also 6×22.4 L of O_2 with glucose gives $= 2822.5$ kJ 21.84 L O_2 with glucose give

$$= \frac{2822 \times 21.84}{6 \times 22.4} = 458.66 \text{ kJ}$$

3. $6C(s) + 3H_2(g) \longrightarrow C_6H_6 \quad \Delta_f H_{(exp)} = -358.5$ kJ

$\Delta_f H_{cal} = \text{BE(Reactants)} - \text{BE(Products)}$

$\text{BE(Reactants)} = 6C_{(s \to g)} + 3(H{-}H)$

$= (6 \times 716.8 + 3 \times 436.9)$

$= 4300.8 + 1310.7 = 5611.5$

$\text{BE(Products)} = 3(C{-}C) + 3(C{=}C) + 6(C{-}H)$

$= 3 \times 340 + 3 \times 620 + 6 \times 490 = 5820$ kJ

$\Delta H_{cal} = 5611.5 - 5820 = -208.5 \text{ kJ mol}^{-1}$

$\text{RE} = \Delta_f H_{(Exp)} - \Delta_f H_{(Cal)}$

$= -358.5 - (-208.5) = -150.0 \text{ kJ mol}^{-1}$

4. $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$

$\Delta H = -5645$ kJ

Moles of O_2 per day $= \frac{640}{32} = 20$ mol O_2

Moles of sucrose used/day $= \frac{20}{12}$ or $\frac{20}{12} \times 342$ g $= 570$ g

$\Delta H = \frac{5645 \times 20}{12} = 9408.34$ kJ

5. The difference in ΔH combustion between CH_4 and C_2H_6 is -157.6 kcal and between C_2H_6 and C_3H_8 is -157.6 kcal (≈ -157.75 average)

i.e. $\Delta_{comb}H$ of $CH_2 = -157.75$

$\Delta_{comb}H(C_8H_{18}) = \Delta_{comb}H(C_3H_8) + 5\Delta_{comb}H(CH_2)$

$= -526.3 + 5 + (-157.75)$

$= -1315.5$ kcal

6. $C = \frac{12}{12} = 1$ mol

$C + O_2 \longrightarrow CO_2; \quad \Delta H_1 = -94.05$ kcal

$x \quad x$

$\underset{(1-x)}{C} + \frac{1}{2}O_2 \longrightarrow \underset{(1-x)}{CO}; \quad \Delta H_2 = -26.41$ kcal

$\therefore x(-94.05) + (1 - x)(-26.41) = -57.5$

$x = 0.46$ mol of CO_2

$1 - x = 0.54$ mol of CO

7.

$$\begin{tikzcd}
CaCl_2(s) \arrow[r, "-75.0"] \arrow[dr, "\Delta H = ?"'] & CaCl_2(aq) \\
& CaCl_2 6H_2O \arrow[u, "+19.0"']
\end{tikzcd}$$

$\Rightarrow -75 = \Delta H + 19 \; \Delta H = -75 - 19$

$= -94 \text{ kJ mol}^{-1}$

In the question, $\Delta_{hyd}H$ from $H_2O(g)$ is to be calculated, whereas $\Delta_{cal}H$ above is from $H_2O(l)$.

$\Delta_{vap}H = 2452 \text{ J g}^{-1} = 2452 \times 18 \text{ J mol}^{-1}$

$= 6 \times 2452 \times 18 \text{ J mol}^{-1}$

$= \frac{6 \times 2452 \times 18}{10^3} \text{ kJ mol}^{-1}$

$= 264.816$

ΔH actual $= -94 - (264.816) = -358.816$ kJ mole^{-1}

8. $XeF_4 \longrightarrow Xe^{\oplus} + F^{\ominus} + F_2 + F$

$Xe \longrightarrow Xe^{\oplus} + e^- $ (IE)

$e^- + F \longrightarrow F^{\ominus}$ (EA) or $\Delta_{eq}H^{\ominus}$

$2F \longrightarrow F_2$ ($\Delta_{diss}H = -ve$)

$\Delta H = (4 \times 34) + (1 \times 279) + (1 \times -38) + 1 \times (-85)$

$= 292$ kJ mol^{-1}

or

$XeF_4(s) \longrightarrow Xe + 4F$ ($\Delta H = 4 \times 34$)

$Xe \longrightarrow Xe^{\oplus} + e^-$ (IE = 279)

$Fe + e^- \longrightarrow F^{\ominus}$ (EA = –85)

$XeF_4 \longrightarrow Xe^{\oplus} + F^{\ominus} + F_2 + F$

$\Delta H = 4 \times 34 + 279 - 85 - 38$

$= 292$ kJ mol^{-1}

9. Let IE $= x$ eV

$E_A = -y$ eV

$\therefore x - y = 0.85$ eV (EA is exothermic)

$\therefore x/y = 7/6$

Solve for x and $y \Rightarrow y = 5.10$ eV

10. Infinitely dilute solutions are completely ionised.

$Ca^{2+}Cl_2^{2-} + Na_2^{2+}CO_3^{2-}$

$\downarrow$

$CaCO_3\downarrow + 2NaCl$

$Ca^{2+} + 2Cl^{\ominus} + 2Na^{\downarrow} + CO_3^{2-}$

$\downarrow$

$Ca^{2+} + CO_3^{2-} + 2Na^{\oplus} + CO_3^{2-}$

$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3(s)$

$-\Delta H^{\ominus} = \Delta_f H^{\ominus} CaCO_3 - [\Delta_f H^{\ominus} Ca^{2+} + \Delta_f H^{\ominus} CO_3^{2-}]$

$= -288.5 - (-129.80 - 161.65)$

$\Delta H^{\ominus} = 2.95$ kcal

11. 1 eV = 96.39 kJ

(1eV $= 1.602 \times 10^{-19}$ J $\times 6.023 \times 10^{-3}$ kJ mol^{-1})

$$\begin{bmatrix} 4eV = 385.92 \text{ kJ} \\ 12eV = 1157.76 \text{ kJ} \end{bmatrix}$$

$X(s) \longrightarrow X(g)$ $\Delta_{sub}H = 100$ kJ

$$\left[\begin{array}{l} X(g) \longrightarrow X^{\oplus}(g) + e^- \quad IE = 385.92 \text{ kJ} \\ X^{\oplus}(g) + aq \longrightarrow X^{\oplus}(aq) \ \Delta H = -380 \text{ kJ} \end{array}\right.$$

$$\begin{array}{c} \hline X(g) \longrightarrow X^{\oplus}(aq) \\ \hline \end{array}$$

$\Delta H = 385.92 - 380 = 5.92$ kJ

Similarly, for $X(g) \longrightarrow X^{2+}(aq)$

$\Delta H = 1157.76 - 1280 = -122.24$ kJ mol^{-1}

Therefore, $X^{2+}(aq)$ is more stable than $X^{\oplus}$ (aq), since ΔH is –ve. More the –ve value, more stable is the ion, in aqueous state.

12. BE of H—H = 104 kcal mol^{-1}

H—H = 2H$^{\bullet}$

$C_6H_5CH_3(g) \longrightarrow C_6H_5\dot{C}H_2 + H^{\bullet}$ ...(i)

$\Delta H = 77.5$

$\Delta H_1 = [\Delta_f H\, C_6H_5\dot{C}H_2 + \Delta_f H\, H^{\bullet}] - [\Delta_f H \text{ (Toluene)}]$

$2(C_6H_5\dot{C}H_2) \longrightarrow C_6H_5—CH_2—CH_2—Ph$ ...(ii)

(Dibenzyl)

$\Delta H_2 = 2_f H(\text{Dibenzyl}) - 2\Delta_f H^{\ominus}(C_6H_5\dot{C}H_2)$

$\Delta_f H^{\ominus} H^{\bullet} = \dfrac{104}{2} = 52$

$\left[\dfrac{1}{2}H_2 \longrightarrow H^{\bullet}\right]$

From reaction (i), $77.5 = (\Delta_f H\,(C_6H_5CH_2) + 52) - 12$

$\Rightarrow \Delta_f H^{\ominus} C_6H_5\dot{C}H_2 = 37.5$ kcal mol^{-1}

From reaction (ii), $\Delta H_2 = (27.8 - 2 \times 37.5)$

$= -47.2$ kcal mol^{-1}

The bond strength of $PhCH_2—CH_2Ph = 47.2$ kcal mol^{-1}

13. **a.** *cis*-2-Butene $\longrightarrow$ *trans*-Butene, ΔH_1

b. *cis*-2-Butene $\longrightarrow$ 1-Butene, ΔH_2

c. *trans*-2-Butane

$+ 6O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(l)$,

$\Delta H = -647.1$ kcal mol^{-1}

d. 1-Butene

$+ 6O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(l)$.

$\Delta H = -649.8$ kcal mol^{-1}

Subtracting equation (*iv*) from (*iii*)

$-647.1 + 649.8 = \Delta_f H(\text{1-Butene})$

$- \Delta_f H(\textit{trans}\text{-2-butene})$

$2.7 = \Delta_f H(\text{1-Butene}) - \Delta_f H(\textit{trans}\text{-2-butene})$

Subtracting equation (i) from (ii), we get

$\Delta H_2 - \Delta H_1 = \Delta_f H(\text{1-Butene})$

$- \Delta_f H(\textit{trans}\text{-2-butene}) = 2.7$

Now, $9\Delta H_1 + 5\Delta H_2 = 0$

$\Delta H_2 - \Delta H_1 = 2.7$

On solving, we get

$\Delta H_1 = -0.96$ kcal

$\Delta H_2 = 1.74$ kcal

14. We have to calculate ΔH for the following equation

$NH_3(g) + H^{\oplus}(g) \longrightarrow 2H(g)$

Given

$H_2(g) + 2H(g) \longrightarrow 2H(g)$ $\Delta H_1 = 218$ kJ mol^{-1}

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ $\Delta H_2 = -46$ kJ mol^{-1}

$NH_4Cl(s) \longrightarrow NH_4^{\oplus}(g) + Cl^{\ominus}(g)$ $\Delta H_3 = 683$ kJ mol^{-1}

$H(g) \longrightarrow H(g)^*$ $\Delta H_4 = 1310$ kJ mol^{-1}

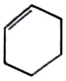
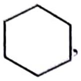
$Cl(g) \longrightarrow Cl^{\ominus}$ $\quad \Delta H_5 = -348 \text{ kJ mol}^{-1}$

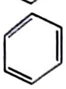
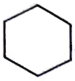
$Cl_2(g) \longrightarrow 2Cl(g)$ $\quad \Delta H_6 = 124 \text{ kJ mol}^{-1}$

$\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(g)$

$\Delta H_7 = -314 \text{ kJ mol}^{-1}$

$$\Delta H = \frac{1}{2}\Delta H_1 - \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 - \frac{1}{2}\Delta H_6 + \Delta H_7$$
$$= -718 \text{ kJ mol}^{-1}$$

15.  $+ H_2(g) \longrightarrow$ , $\Delta H = -119 \text{ kJ mol}^{-1}$

 $+ 3H_2(g) \longrightarrow$ , $\Delta H = -3 \times 119 \text{ kJ mol}^{-1}$

$-357 = \Delta_f H^{\ominus} C_6H_{12}(l) - \Delta_f H^{\ominus}(\text{benzene})$

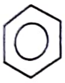
$\Delta_f H^{\ominus}$ (benzene) $= -156 + 357 = 201 \text{ kJ mol}^{-1}$

Resonance energy $= \Delta_f H^{\ominus}(\text{benzene}) - \Delta_f H^{\ominus}(\text{benzene})$

Actual **Theoretical**

$\Delta_f H^{\ominus}$ (benzene) $= -156 + 201 = 49 \text{ kJ mol}^{-1}$

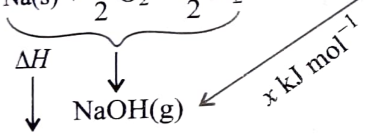
Actual

 $(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2(l)$

$$\Delta H^{\ominus} = 6\Delta_f H^{\ominus}CO_2(g) + 3\Delta_f H^{\ominus}H_2O\ (l) - \Delta_f H^{\ominus}(\text{benzene})$$
$$= 6(-393.5) + 3(-285.8) - 49 = -3267.4 \text{ kJ mol}^{-1}$$

16. Given

$Na(s) + \frac{1}{2}O_2 + \frac{1}{2}H_2 \longrightarrow NaOH(s); \Delta H = -427 \text{ kJ}$



Calculated as follows

$$= \left[\Delta H_{\text{sub(Na)}} + \frac{1}{2}\Delta H_{O_2(\text{diss})} + \frac{1}{2}\Delta H_{H_2(\text{diss})}\right]. - \left[\Delta H_{\text{NaOH(diss)}} + \Delta H_{\text{OH(diss)}}\right]$$

$$= \left(109 + \frac{251}{2} + \frac{435}{2}\right) - (255 + 465) = -268 \text{ kJ mol}^{-1}$$

Now, $-268 = -427 + x$

$\Rightarrow x = +159 \text{ kJ mol}^{-1}$

Exercise 6.4

1. $\Delta_{\text{melting}}S = \dfrac{\Delta_{\text{melting}}H}{T}$

or $T = \dfrac{\Delta_{\text{melting}}H}{\Delta_{\text{melting}}S} = \dfrac{30 \times 10^3}{15} = 2 \text{ kJ}$

2. $\Delta_r S^{\ominus} = S^{\ominus}(NH_2CONH_2) + S^{\ominus}(H_2O) - [2S^{\ominus}(NH_3) + S^{\ominus}(CO_2)]$

$= 174.0 + 69.9 - [2 \times 192.3 + 213]$

$= -354.4 \text{ J K}^{-1} \text{ mol}^{-1}$

3. **a.** $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$= 2S^{\ominus}[CO_2(g)] - \{2S^{\ominus}[CO(g) + S^{\ominus}[O_2(g)]\}$

$= 2(213.6) - \{2(197.6) + (205.03)\}$

$= 427.2 - 600.23$

$= -173.03 \text{ J K}^{-1}$

b. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$\Delta S^{\ominus} = \{2S^{\ominus}[H_2O(l)]\} - \{2S^{\ominus}[H_2(g)] + S^{\ominus}[O_2(g)]\}$

$= 2(69.96) - \{2(130.6) + 205.03\}$

$= 189.92 - 466.23$

$= -326.31 \text{ J K}^{-1}$

4. **b.** $\Delta S = +ve$

5. **b.** $\Delta S = \dfrac{q_{\text{rev}}}{T}$

6. **a.** $\Delta G = 0$

7. **c.**

Exercise 6.5

1. $\Delta H =$ Lattice energy – Hydration energy

$= 777 - 774 = 3 \text{ kJ mol}^{-1}$

$\Delta G = \Delta H - T\Delta S = 3 - 298\ (40 \times 10^{-3})$

$= -392 \text{ kJ mol}^{-1}$

2. $\Delta G^{\ominus}$ for the reaction:

$\Delta G^{\ominus} = \Delta_f G^{\ominus}(C_6H_6) - 3[\Delta_f G^{\ominus}(HC \equiv CH)]$

$= 1.24 \times 10^5 - 3 \times 2.09 \times 10^5$

$= -5.03 \times 10^5$

Now, $\Delta G^{\ominus} = -2.303RT \log K$

or $\log K = -\dfrac{\Delta G}{2.303\,RT}$

$= -\dfrac{-5.03 \times 10^5}{2.303 \times 8.314 \times 298} = 88.155$

$\therefore$ $K = \text{Antilog}(88.155) = 1.43 \times 10^{88}$

Since value of ΔG is negative, the reaction is feasible and may be recommended for making benzene.

3. **a.** Since $\Delta H = -ve$, exothermic process and is favoured, i.e., it will be spontaneous.

b. $\Delta G = \Delta H - T\Delta S$

$= -270.6 \times 1000 - 300 \times (-139)$

$= -228900 \text{ J} = -228.9 \text{ kJ}$

4. $\Delta G^{\ominus}$ can be calculated by using:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta H^{\ominus} = \Sigma(\text{BE})(\text{reactants}) - \Sigma(\text{BE})(\text{products})$

$= 435 + 240 - 2 \times 430 = -185 \text{ kJ}$

$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$= 2 \times 186.68 - 130.59 - 222.95$

$= 19.82 \text{ JK}^{-1} = 19.82 \times 10^{-3} \text{ kJ K}^{-1}$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= -185 - 298 \times 19.82 \times 10^{-3} = -190.9 \text{ kJ}$

5. For nC_4H_{10},

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= -124.73 - 298(-365.8 \times 10^{-3})$

$= -15.72$ kJ

For isobutane (iso-C_4H_{10}),

$\Delta G^{\ominus} = -131.6 - 298(-381.079 \times 10^{-3}) = -18.04$ kJ

For conversion of $nC_4H_{10} \longrightarrow$ iso-C_4H_{10},

$\Delta G^{\ominus} = -18.04 - (-15.72) = -2.32$ kJ

Negative value shows that the process is spontaneous.

6. a. ΔG is +ve if ΔH is +ve and ΔS is –ve. Thus, reaction is non-spontaneous.

Hence, (a) is the correct answer.

7. $\Delta S^{\ominus} = 2S^{\ominus}(\text{HI}) - [S^{\ominus}(H_2) + S^{\ominus}(I_2)]$

$= 165.3\ \text{JK}^{-1}\ \text{mol}^{-1}$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= 51.9 \times 10^3 - 298(165.3) = 2.641\ \text{kJ mol}^{-1}$

Exercises

Single Correct Answer Type

1. (2) i. $H^{\oplus} + \overset{\ominus}{O}H \longrightarrow H_2O \qquad \Delta H_1 = -13.4$ kcal

ii. $\overset{\ominus}{O}H + HF \longrightarrow H_2O + F^{\ominus} \qquad \Delta H_2 = -16.4$ kcal

iii. $HF \longrightarrow H^{\oplus} + F^{\ominus} \qquad \Delta H_3 = ?$

$\Delta H_3 = \Delta H_2 - \Delta H_1$

$= -16.4 - (-13.4) = -3.0$ kcal

2. (2) $\Delta H = \Delta U + \Delta n_g RT$

$= 2.1 \times 2 \times 0.002 \times 300 = 3.3$ kcal

$\Delta G = \Delta H - T\Delta S$

$= 3.3 \times -300 \times (0.02) = -2.7$ kcal

3. (1) $\Delta G = \Delta H - T\Delta S = -\text{ve}$

All exothermic reactions are spontaneous, hence HF will attack SiO_2.

4. (3) On comparison:

$$\Delta S = -\left[\frac{d(\Delta G)}{dT}\right]$$

$$\Delta S = -\frac{d(-nFE)}{dT} = nF\left(\frac{dE}{dT}\right) \qquad \left[\begin{array}{l}\text{Here } E \text{ is the} \\ E_{mf} \text{ of cell}\end{array}\right]$$

$$\therefore \left(\frac{dE}{dT}\right) = \frac{\Delta S}{nF}$$

5. (4)

6. (3) V_1 (volume of 1 g H_2) = 11.2 L at STP

V_2 (volume of 1 g H_2) = 22.4 L

$\therefore W = P\Delta V = 11.2$ L atm

7. (1) $T_2 = T_1\left(\dfrac{V_1}{V_2}\right)^{\gamma - 1} = 150$ K

$w = -C_V\Delta T = -C_V(T_2 - T_1)$

$= -3 \times 2 \times (150 - 300)$

$= 900$ cal

8. (2) $W = P(\Delta V)$

$PV = RT$

$P(V + \Delta V) = R(T + 1)$

$\therefore P\Delta V = R$

9. (4) $\underset{27\text{ g}}{Al} + \dfrac{3}{2}O_2 \longrightarrow \underset{51\text{ g}}{\dfrac{1}{2}Al_2O_3}$

$\Delta H = -837.8\ \text{kJ mol}^{-1}$

(1) 0.624 mol of Al = 837.8 × 0.624 on combustion gave = 523 kJ.

Hence false.

(2) Formation of 0.624 mol of Al_2O_3 gave

= 837.8 × 2 × 0.624

= 1045 kJ

Hence, false.

(3) 0.312 mol of Al on combustion gave = 261 kJ. Hence, false.

(4) Formation of 0.150 mol of Al_2O_3 gave = 251.3 kJ. Hence, true.

10. (3) $PV = RT$ at temperature T for one mol

$P(V + \Delta V) = R(T + 1)$ at temperature $(T + 1)$ for one mol

$\therefore P\Delta V = R$

11. (4) $\eta = \dfrac{T_2 - T_1}{T_2}$; T_1 = temperature of sink

T_2 = temperature of the source

$0.25 = \dfrac{T_2 - T_1}{T_2}$

12. (1) Oxalic acid has two ionisable $H^{\oplus}$. Hence, expected heat of neutralisation, if it behaves as a strong acid would have been

$= -13.7 \times 2 = -27.4\ \text{kcal mol}^{-1}$

But experimental value $= -25.4\ \text{kcal mol}^{-1}$

$\therefore$ Heat of ionisation $= 2.0\ \text{kcal mol}^{-1}$

13. (3) $\Delta U = q - w = q - P\Delta V$

$= 200 - 2 \times 10^5 \times 500 \times 10^{-6}$

$= 100$ J

14. (2)

15. (3) In an ideal gas, there is no force of attraction between molecules. Hence, no heat is lost in the expansion.

16. (2) $H^{\oplus} + \overset{\ominus}{O}H \rightleftharpoons H_2O$

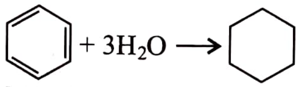
$\Delta H = -13.7$ kcal

$\Delta H^{\ominus} = \Delta_f H^{\ominus}(H_2O) - [\Delta_f H^{\ominus}(H^{\oplus}) + \Delta_f H(\overset{\ominus}{O}H)]$

$= -68 - (0 - 13.7) = -54.3\ \text{kcal mol}^{-1}$

$[\Delta_f H^{\ominus}(H^{\oplus}) = 0(\text{convention})]$

17. (3) $CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3 \qquad \Delta H = x_1$



$\Delta H = x_2$

RE $= 3x_1 - x_2$

18. (3) $\Delta H = 2.303\,R\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]\log\dfrac{P_2}{P_1}$

$460.6 = 2.303 \times 2\left[\dfrac{1}{50} - \dfrac{1}{T_2}\right]\log 10$

$\therefore T_2 = 100$ K

19. (3) $\Delta H = (\text{BE})_{\text{reactant}} - (\text{BE})_{\text{products}}$
[But all the species must be in gaseous state. In product, $[\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(g)}]$ ΔH must be added.

Hence, $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)}$

$$\Delta H = \left[(\text{BE})_{\text{H—H}} + \frac{1}{2}(\text{BE})_{\text{O=O}}\right]$$
$$= [(\Delta H)_{\text{vap}} + 2(\text{BE})_{\text{O—H}}]$$
$$= x_1 + \frac{x_2}{2} - [x_4 + 2x_3]$$
$$= x_1 + \frac{x_2}{2} - x_4 - 2x_3$$

20. (2)

21. (2)

22. (2) i. $\text{Mg(s)} + \text{Cl}_2\text{(g)} \longrightarrow \text{MgCl}_2\text{(s)}$ $\quad \Delta H_1 = -642$

ii. $\text{Mg(s)} + \frac{1}{2}\text{Cl}_2\text{(g)} \longrightarrow \text{MgCl(s)}$ $\quad \Delta H_2 = -125$

iii. $2\text{MgCl} \longrightarrow \text{MgCl}_2 + \text{Mg}$ $\quad \Delta H = ?$

$\Delta H = \Delta H_1 - 2\Delta H_2$
$= -642 - 2 \times (-125) = -392 \text{ kJ mol}^{-1}$

23. (2) $\text{CO}_2\text{(g)}$, $\text{H}_2\text{O(l)}$, and $\text{SO}_2\text{(g)}$.

24. (4) In enthalpy of formation, reactants and products must be in most stable standard state.

25. (3) Combustion of one mole of reactants gives products in standard state or most stable state.

26. (3) $\Delta H = \Delta U + \Delta nRT$
$\Delta n = n_P - n_R$

$\therefore \Delta n = 2 - \frac{5}{2} = -\frac{1}{2}$

$\therefore \Delta H = \Delta U - \frac{1}{2}RT$

$\therefore \Delta U = \Delta H + \frac{1}{2}RT$

or $\therefore \Delta U > \Delta H$

27. (2) $\Delta H_1 > \Delta H_2$

28. (4)

29. (3) Standard state implies to 1 atm pressure and 298 K temperature.

30. (2) $\Delta H = \Delta U + \Delta nRT$
In (2), $\Delta n = 0$
$\therefore \Delta H = \Delta U$

31. (2) $H = U + PV$

32. (3) $\Delta H = \Delta U + \Delta(PV)$
$= \Delta U + \Delta P\,\Delta V$

33. (3) $\Delta_f H^\ominus = (\Delta_f H^\ominus{}_P - \Delta_f H^\ominus{}_R)$

34. (2) $\Delta H = \Delta U + P\,\Delta V$

35. (3) $q_P = q_V$

36. (2) $\Delta G = \Delta H - T\,\Delta S$

37. (2) $\Delta H > \Delta E$
$\text{C}_4\text{H}_{10} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$

38. (4) Entropy depends upon pressure, volume, and temperature.

39. (1) $\Delta H = \Delta U + \Delta nRT$
$\Delta n = n_P - n_R = 2 - 1 = 1$
$\therefore \Delta H = \Delta U + (1)RT$
$\therefore \Delta H > \Delta U$

40. (4) $\Delta S = \frac{q_{\text{rev}}}{T}$

41. (1) $G_{\text{(ice)}} = G_{\text{(water)}} = 0$

42. (4)

43. (4) $\Delta H = \Delta U + \Delta nRT$
$\Delta n = 0 = n_P - n_R$
$\therefore \Delta H = \Delta U$

44. (3) $w = P_{\text{ex}}(\Delta V)$

45. (3) $\Delta S_{\text{total}} = 0$

46. (2) At equilibrium, $\Delta S_{\text{total}} = 0$
$\therefore S_P^\ominus - S_R^\ominus = 0$

47. (3)

48. (1)

49. (2)

50. (2) Evaporation of water required heat energy to proceed the reaction.

51. (1) Dissociation of CaCO_3 required energy.

52. (1)

53. (2)

54. (3)

55. (4)

56. (2) By definition $C_{P,m} = \frac{dq_P}{dT}$

For $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O(s)}$,
temperature does not change if some heat is given to the system. Hence

$$C_{P,m} = \frac{+\text{ve}}{\text{Zero}} = \infty$$

57. (4) Standard molar enthalpy of formation CO_2 and the standard molar enthalpy of combustion of carbon (graphite) refer to the same chemical equation:
$\text{C(graphite)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$

58. (3)

59. (1)

60. (2, 4)

61. (2) $\text{C}_2\text{H}_5\text{SH} + \frac{9}{2}\text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O(l)} + \text{SO}_2\text{(g)}$

62. (4)

Multiple Correct Answers Type

1. (2, 4)
$\Delta G = -$ve for spontaneous process and $\Delta G^\ominus \neq 0$ at equilibrium. Statement (b) represents Carnot theorem.

2. (2, 3, 4)
Mass-independent properties are intensive.

3. (1, 3)
Mass-dependent properties are extensive.

4. (1, 2, 3)
For a cyclic process, $dU = 0$
$\therefore q = \Delta U + (-w) \Rightarrow q = -w$
Also, w = Area covered by sphere

$$= \pi r^2 = \pi \times \left[\frac{(V_2 - V_1)}{2}\right]^2$$
$$= \frac{\pi \times (20)^2}{2^2}$$
$$= 100\pi = 100 \times 3.14 = 314 \text{ J}$$

5. (1, 2, 3)

The correct order is $w_3 > w_1 > w_2 > w_4$.

6. (1, 3)

γ for mono-atomic is 1.66.

$$\therefore C_V = \frac{3R}{2}, C_P = \frac{5}{2}R$$

$$C_{VM} = \frac{2 \times \frac{3R}{2} + 2 \times \frac{3R}{2}}{4} \quad \therefore C_V = 3 \text{ cal}$$

$$C_{PM} = \frac{2 \times \frac{5R}{2} + 2 \times \frac{5R}{2}}{4} \quad \therefore C_P = 5 \text{ cal}$$

7. (2, 3, 4)

$\Delta G^\ominus = 0$ at equilibrium under standard state. Also, at equilibrium, $\Delta G = 0$.

$\therefore \Delta H^\ominus - T\Delta S^\ominus = 0$

Also, $\Delta G^\ominus = 2.303RT \ln K$

$\therefore K = 1$

8. (1, 2, 3, 4)

$$\frac{C_P}{C_V} = 1.4 = \gamma$$

$$C_P - C_V = R$$

$$\therefore C_V = \frac{R}{\gamma - 1} \text{ and similarly } C_P - \frac{C_P}{\gamma} = R$$

$$\therefore C_V = \frac{2}{0.4} = 5 \text{ cal} \quad \therefore C_P = \frac{\gamma . R}{(\gamma - 1)}$$

$$\text{Also, } C_V = \frac{2}{0.4 \times 32} = 0.156 \text{ cal}$$

9. (1, 2, 3, 4)

These are mathematically established facts.

10. (2, 3, 4)

$H_2O(s)$ has more ordered arrangement. Also, $\Delta S^\ominus_2$

$$= S^\ominus_{H_2O}(l) - S^\ominus_{H_2O}(l)$$

$$\Delta S_1^\ominus = S^\ominus_{H_2O}(l) - S^\ominus_{H_2O}(s)$$

$\because S^\ominus_{H_2O(v)}$ is maximum and thus $\Delta S^\ominus_2 >>> \Delta S^\ominus_1$.

11. (2, 4)

Intensive property does not depend upon the mass of substance.

12. (1, 3)

13. (1, 2)

14. (4) Use Hess' law.

15. (1, 2, 3)

The sum of two extensive properties is always extensive while the ratio of extensive properties is intensive and the derivation is also intensive.

16. (1, 2, 3)

The multiplication of two intensive properties is an intensive property and their ratio and derivative is also an intensive property.

17. (1, 2)

$\Delta U = 0$ for cyclic and isothermal process.

18. (1, 2, 3, 4)

19. (1, 2, 3)

$\Delta G^\ominus = -RT \ln K_p$ or $K_p = e^{-\Delta G^\ominus/RT}$

20. (1, 3)

$$\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = R$$

21. (2, 3, 4)

In endothermic reaction, heat is absorbed by the system from the surroundings.

22. (1, 2) In isothermal process $\Delta T = 0$ and $\Delta U = \Delta H = 0$

23. (2, 3)

$\Delta H = \Delta U + \Delta nRT$, where $\Delta n = n_P - n_R$

(n = number of moles)

24. (2, 3, 4)

25. (1, 2)

For spontaneous process, $\Delta G = -$ve and $\Delta S_{\text{Total}} = +$ve

26. (1, 3)

27. (1, 2)

In adiabatic process, $q = 0$. Hence, in expansion process, temperature decreases and hence internal energy also decreases.

28. (1, 2) **29. (1, 2)**

30. (1, 2, 3) **31. (2, 3, 4)**

32. (1, 2, 3) Mathematical relation

33. (1, 2, 4)

In conversion of solid ice to liquid and in rusting, the entropy increases.

34. (1, 3, 4) **35. (1, 2, 3, 4)**

36. (1, 2) **37. (1, 2, 3, 4)**

In all these process heat of reaction changes

38. (1, 2, 3, 4) Born-Haber cycle

39. (1, 3)

40. (1, 2, 3)

Hess' law can be used for all these process or reaction.

41. (2, 3, 5)

In spontaneous process, $\Delta G = -$ve, $\Delta H = -$ve, and $\Delta S = +$ve

42. (2, 4)

$\Delta G = \Delta H - T\Delta S$ for spontaneous process ΔG must be negative. When $\Delta H = +$ve or endothermic then to make $\Delta G = -$ve. Temperature should be high.

43. (3, 4)

44. (1, 3, 4)

45. (1, 2, 3)

In open system, heat and matter can be exchanged between system and surrounding.

46. (1, 3)

47. (2, 4)

The first law of thermodynamics states that $\Delta U = q + w$, i.e., the internal energy of system is equal to the sum of heat and work.

48. (1, 2, 4)

In all these conversion, the degree of randomness decreases.

49. (2, 3)

50. (1, 2, 3, 4)

The heat of neutralization for strong acid and base is equal to −57.3 kJ mol^{-1} or −13.7 kcal mol^{-1}.

51. (2, 3)

$C(graphite) \longrightarrow C(g)$. The process is sublimation as well conversion of crystalline allotropic from (graphite) to amorphous form (gas carbon).

52. (1, 2, 3)

In (a), volume change is negligible while in (b) and (c), there is no volume change.

Linked Comprehension Type

1. (2) $\Delta G = \Delta H - T\Delta S$, at high temperature $T\Delta S$ factor dominates of ΔH and hence ΔG becomes negative and reaction occurs spontaneously.

2. (1) $\Delta G = \Delta H - T\,\Delta S$

When $\Delta H = 2.0$ kcal $= 2000.0$ cal

$\Delta S = 20$ cal K^{-1}

$T = 298$ K

$\Delta G = 2000.0 - 298 \times 20$ cal K^{-1}

$= -3960.0$

$= -ve$, hence spontaneous.

3. (3) $\Delta G = \Delta H - T\,\Delta S$

For spontaneous process, $\Delta G = -ve$

or $\Delta H < T\,\Delta S$

$$\therefore\ T > \frac{\Delta H}{\Delta S} = \frac{100\ \text{Kcal}}{0.02\ \text{Kcal K}^{-1}} = 5000\ \text{K}$$

4. (4) Use $\Delta G = \Delta H - T\,\Delta S$ equation

5. (1) $\Delta G = \Delta H - T\,\Delta S$

$= -15.0$ kcal $mol^{-1} - 300 \times (-7.2$ cal K^{-1} $mol^{-1})$

$= -12.84$ kcal mol^{-1}

6. (2) $\Delta G = G_P - G_R$

$= -19.7$ kcal mol^{-1}

7. (2)

$$\begin{array}{lll} & A(s) \longrightarrow A(l); & \Delta H = x \\ & A(l) \longrightarrow A(g); & \Delta H = y \\ \hline \text{On addition} & A(s) \longrightarrow A(g); & \Delta H = x + y \\ \hline \end{array}$$

8. (4)

$$\begin{array}{ll} & H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(l);\ \Delta H = -68.00\ \text{kcal} \\ & H_2O(l) \longrightarrow H_2O(g);\ \Delta H = 10.0\ \text{kcal} \\ \hline \text{On addition} & H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(g);\ \Delta H = -58.0\ \text{kcal} \\ \hline \end{array}$$

9. (1)

$C(g) + O_2 \longrightarrow CO_2(g);\ \Delta H = -y$ ...(i)

$C(d) \longrightarrow C(g);\ \Delta H = -1.89$ kJ ...(ii)

Adding equations (i) and (ii), we get

$C(g) + C(d) + O_2 \longrightarrow CO_2 + C(g);\ \Delta H = -y + 1.89$ kJ

or $C(d) + O_2 \longrightarrow CO_2;\ \Delta H = -y + 1.89$ kJ

Hence, the combustion of diamond releases energy less than 1.89 kJ.

10. (4) Graphite is a standard state of carbon and CH_3OH in liquid state is also standard state.

11. (2) $H = U + PV$

12. (2) $\Delta H = \Delta U + \Delta nRT$

$\therefore\ \Delta U = \Delta H - \Delta nRT$

13. (4) According to the first law of thermodynamics

$\Delta U = q - w$

In isothermal process, $\Delta U = 0$

$\therefore\ q = w$

or $w = nRT_1 \ln\frac{V_2}{V_1}$

14. (2) Path $(B + C)$ occurs in adiabatic conditions

$\therefore\ q = 0$

We know that

$\Delta S = \frac{q_{rev}}{T}$

$\therefore\ q_{rev} = T\,\Delta S$

$\therefore\ q_{rev} = nR \ln\frac{V_2}{V_1}$

15. (1) For path A

$$\Delta S = \frac{q_{rev}}{T} = \frac{nRT_1}{T_1}\ln\frac{V_2}{V_1} = nR\ln\frac{V_2}{V_1}$$

16. (1) $w = q = P_1(V_2 - V_1)$

17. (4) For path $(D + E)$

$\Delta S = nR\ln\frac{V_2}{V_1}$

18. (1) $\Delta H^\ominus = \Delta H^\ominus_P - \Delta H^\ominus_R$; (for 1 mol)

$$= \left[-1575.0\ \text{kJ mol}^{-1} - \frac{3}{2} \times 241.8\right] - [-2021.0\ \text{kJ mol}^{-1}]$$

$= +83.3$ kJ mol^{-1}

For 1 kg $CaSO_4 \cdot 2H_2O$

Number of moles $= \frac{1000}{172} = 5.81$

$\therefore$ Heat change for 5.81 mol of $CaSO_4 \cdot 2H_2O$

$= 5.81 \times 83.3$ kJ mol^{-1}

$= 484$ kJ mol^{-1}

19. (2) $\Delta G = \Delta H - T\,\Delta S$

$= 17.92$ kJ $\qquad (\Delta S = S_P - S_R)$

20. (2) $\Delta G = -nRT \ln K$

$\therefore\ K = e^{-\Delta G/nRT}$

21. (4) $\Delta G = -nRT \ln K_P$

or $K_P = e^{-\Delta G/nRT}$

22. (2) Because $\Delta H = +ve$ and $\Delta G = +ve$

23. (2) Work in reversible isothermal expansion is greater than work done in adiabatic expansion.

24. (1) $P_1V_1 = P_2V_2$ (Boyle's law)

25. (2) **26. (4)** **27. (3)**

28. (4) $\Delta H = -\text{ve}$ and $\Delta S = +\text{ve}$, both favour the process.

29. (4) $\Delta G = \Delta H - T\Delta S$ can be negative at ordinary temperature T if ΔH is –ve and ΔS is +ve.

30. (4) At equilibrium, $\Delta G = 0$

Hence, $0 = \Delta H - T\,\Delta S$

or $\Delta H = T\,\Delta S$

31. (2) For endothermic reaction, ΔH = +ve. As $\Delta G = \Delta H - T\,\Delta S$, is +ve at low temperature if ΔS is positive but $T\,\Delta S < \Delta H$. At high temperature, $T\,\Delta S > \Delta H$ and ΔG become –ve.

32. (3)

33. (2) Expansion from state A to state B occurs at constant pressure (isobaric expansion) = $2P$

34. (3) Expansion from state D to state A occurs at constant volume (isochoric process) = V

35. (1) Work done = $-P\,\Delta V$

or $-P(2V - V) = -PV$

36. (4) In conversion from B to C, volume does not change or $\Delta V = 0$, therefore $w = 0$.

37. (4) $q = -w$

$\therefore q = PV$

38. (3) In expansion of CO_2 gas molecule, entropy of *system* $\Delta_{sys}S$ increases or $\Delta_{sys}S > 0$ and entropy of surrounding decreases $\Delta_{surr}S < 0$.

39. (1) – Work done = $q = nRT \ln \frac{V_2}{V_1}$

$$= 3 \times 8.314 \times 288.15 \times \ln\left(\frac{30}{10}\right)$$

$$\therefore \Delta S = \frac{q}{T}$$

$$\text{or } \Delta_{sys}S = \frac{3 \times 8.314 \times 288.15 \times \ln\frac{30}{10}}{288.15} = 27.4 \text{ J K}^{-1}$$

40. (4) **41. (3)** **42. (1)**

43. (4) In cyclic process, $\Delta H = 0$.

44. (2) In expansion from state 1 to state 2.

$P = 1$ atm

$V_1 = 22.44$ L

$V_2 = 44.88$ L

$C_V = \frac{3}{2}R$

$\Delta T = T_2 - T_1 = 546 - 273 = 273$ K

$$\therefore \Delta U = nC_V\,\Delta T = 1 \times \frac{3}{2} \times 8.314 \times 273 = 3.40 \times 10^3 \text{ J}$$

45. (3) In conversion from state 2 to state 3

$\Delta T = T_2 - T_1 = 273 - 546 = -273$ K

$C_V = \frac{3}{2}R$

$$\therefore \Delta U = nC_V\,\Delta T = 1 \times \frac{3}{2} \times 8.314 \times (-273)$$

$= -3.40 \times 10^3$ J

46. (4)

47. (4) $\Delta U = nC_V\, dT$

moles $(n) = \frac{0.1\text{ g}}{16} = 6.25 \times 10^{-3}$

$C_V = 500 \text{ J K}^{-1}$

$T = 273 + 2 = 275$ K

$\therefore \Delta U = -160$ kJ

48. (2) $\Delta H = \Delta U + \Delta nRT$, where Δn = change in number of moles. Here, in given reaction, $\Delta n = 0$.

$\therefore \Delta H = \Delta U$

49. (3)

50. (2) Heat released to cool 500 g water from 20°C to 0°C.

$q = ms\,\Delta T$

$= 500 \times 4.18 \times 20 = 41800$ J

$= 41.8$ kJ

Number of moles of water (ice) that will melt to absorb

$41.8 \text{ kJ} = \frac{41.8}{6.02} \approx 7$

Therefore, number of cubes of ice that will melt = 7.

51. (1) Fluorine is more electro-negative than oxygen and oxygen is more electro-negative than nitrogen and hence bond energy between F—H in greater than O—H which is greater than N—H.

52. (2) Bond energy of F_2 is surprisingly low due to strong repulsion between the lone pairs of two fluorine atoms.

53. (2)

54. (2) Average bond energy is considered.

55. (1) $\Delta H = H_P - H_R$

56. (1) $\Delta H = H_P - H_R$

57. (1) $\Delta G = \Delta H - T\,\Delta S$

58. (1) $\Delta G = -nRT \ln K$

$\Delta G = -nFE^{\ominus}$

59. (1) $(\Delta G)_{T,P} = 0$

60. (3) $\Delta G = \Delta H - T\,\Delta S$

61. (2) $\Delta G = \Delta H - T\,\Delta S$

ΔG = –ve at high temperature

62. (2) Isochoric process ($\Delta V = 0$)

63. (2) $P = \frac{nRT}{V}$

64. (2) $w = nRT \ln \frac{V_2}{V_1}$

65. (3) Isobaric process ($\Delta P = 0$)

66. (1) $P_1 = \frac{nRT_1}{V_1}$; $V_1 = 20$ L; $T = 200$ K

$P_2 = \frac{nRT_2}{V_2}$; $V_2 = 20$ L; $T = 400$ K

67. (1) In adiabatic process, $q = 0$

and $\Delta S = \frac{q}{T}$

$\therefore \Delta S = 0$

68. (3) **69. (2)**

70. (4) $\Delta S = \dfrac{\Delta H}{T}$

71. (2) $\Delta S = 2.303 C_P \log_{10}\left(\dfrac{V_1}{V_2}\right)$

$= C_P \ln_{10}\left(\dfrac{V_1}{V_2}\right) = C_P \ln_e\left(\dfrac{1}{1/2}\right)$

$= C_P \ln_e 2$

72. (4) w = Work done = Area under curve

73. (1)

74. (3) Slope of the adiabatic curve $\propto \gamma$

Slope of B > slope of A

He ($\gamma = 1.66$); $O_2(\gamma = 1.44)$

75. (1) $w = -2.303\ nRT \log\left(\dfrac{P_1}{P_2}\right)$

$= -2.303 \times 1 \times 8.314 \times 273 \log\left(\dfrac{1}{0.1}\right) = -5.227$ kJ

$q = -w = +5.227$ kJ for isothermal process

76. (2)

Matrix Match Type

1. (a → r) $\Delta G = -$ve, Gibbs free energy is negative and it favours the reaction to occur spontaneously.

(b → s) Endothermic reaction $\Delta H = H_P - H_R > 0$. Therefore, $H_P > H_R$.

(c → p) Bond enthalpy $= \Sigma(\text{BE})_R - \Sigma(\text{BE})_P$

(d → q) For solid and liquid $\Delta H = \Delta U = 0$

2. (a → t) For ideal gas, $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$

(b → r) In adiabatic process, $q = 0$. Therefore, from the first law of thermodynamic, $\Delta U = q - w$ and $q = 0$

$\therefore\ \Delta U = -w.$

(c → p) In isothermal process, $\Delta U = 0$, because internal energy is the function of temperature.

(d → q) $\Delta G^{\ominus} = -nFE^{\ominus}$

(e → s) $\left(\dfrac{\partial T}{\partial P}\right)_H \neq 0$ for real gases.

3. (a → s)

(b → r) Kirchoff's equation relate the variation of enthalpy with temperature.

(c → p) For ideal gas, $\left(\dfrac{\partial U}{\partial V}\right)_T = 0.$

(d → q) Inversion temperature, $T_i = \dfrac{2a}{Rb}$

4. (a → p)

(b → u) Kirchoff's equation $\Delta H = \Delta C_P(T_2 - T_1)$

(c → s) Dissolution of $H^{\oplus}$ in water is non-spontaneous for this reaction $\Delta G > 0$

(d → t) For spontaneous process, entropy always increases, i.e, $\Delta S^{\ominus} > 0$

5. (a → p, r; b → p; c → q; d → p, r, s)

6. (a → p, r) Kirchoff's equation $\Delta H = \Delta C_P(T_2 - T_1)$

(b → q, r) $\Delta U = \Delta C_V(T_2 - T_1)$

(c → p) $\dfrac{\Delta H}{T} = \Delta S$

(d → s) The third law of thermodynamics states that at absolute zero the entropy of a perfectly cyrstalline substance is zero.

7. (a → q)

(b → p, r)

(c → p, r)

(d → p, r, s) Kirchoff's relation $\Delta H = C_P\ \Delta T$

8. (a → p, q) Specific heat = Amount of heat required to raise temperature of 1 mol substance.

(b → q, p) C_P or $C_V = \dfrac{\Delta H}{\Delta T}$ or $\dfrac{\Delta U}{\Delta T}$

(c → s)

(d → r)

9. (a → q) $\Delta_{\text{total}}S > 0$ is according to second law of thermodynamics. It states entropy of universe is continuously increasing due to spontaneous processes taking place in it.

(b → r) If $\Delta_{\text{total}}S < 0$, the process is non-spontaneous. $\Delta_{\text{total}}S$ means $\Delta_{\text{sys}}S + \Delta_{\text{surr}}S > 0$, for a spontaneous process.

(c → s) $\Delta H = \Delta U + \Delta nRT$

(d → p) $-\Delta G = W_{\text{useful}}$, i.e., useful work done by the system.

i.e., decrease in free energy is measure of useful work done by the system.

10. (a → s) Hess' law states that enthalpy change in a reaction remains the same whether the reaction takes place in one step or in several steps.

(b → r) Combustion reactions are exothermic.

(c → q) $\dfrac{\Delta_{\text{vap}}H}{\text{Boiling point in K}} = 88\ \text{J K}^{-1}\ \text{mol}^{-1}$

(d → p) $2.303 \log\dfrac{P_2}{P_1} = \dfrac{\Delta_{\text{vap}}H}{R}\left(\dfrac{T_2 - T_1}{T_1T_2}\right)$

It is Clausius–Clapeyron equation.

11. (a → r) Enthalpy is a states function and is a function of internal energy and pressure and volume.

(b → p) Temperature is independent of the bulk matter of the system and hence it is a intrinsic property but it is a state variable.

(c → r) Free energy is a state function as it depends on the state of the system as well as it depends on H, T and S. It is also a function of U, P, V.

(d → q) Work is a path function as the amount of work done depends upon path undertaken.

12. (a → s) Whenever internal energy of a system decreases, then the temperature always decreases.

In an adiabatic expansion work is done by the gas

$\Rightarrow w$ is $-$ve

$\Rightarrow \Delta U = -$ve

$\Rightarrow$ Temperature decreases

(b → r) For an ideal gas, $\left(\frac{\partial E}{\partial V}\right)_T = 0$

(c → q) Whenever internal energy increases temperature of the system increases.

(d → p) During resonance,

$\Delta H_{\text{Combustion (experimental)}} < \Delta H_{\text{Combustion (calculated)}}$.

Similarly,

$\Delta H_{\text{Combustion (experimental)}} < \Delta H_{\text{Combustion (calculated)}}$ in $CH_2{-}CH{-}CH{=}CH_2$ where resonance takes place.

13. (a → s) $dU = \left(\frac{dU}{dV}\right)_T dV + \left(\frac{dU}{dT}\right)_V dT$

For an ideal gas $\left(\frac{dU}{dV}\right)_T = 0$

$\Rightarrow dU\left(\frac{dU}{dT}\right)_V dT$

But for isothermal expansion/compression of ideal gas, $dT = 0$

$\Rightarrow dU = 0$

$H = U + PV$

$\Rightarrow \Delta H = \Delta U + \Delta(PV);\quad \Delta U = 0$

and $PV =$ constant for isothermal change

$\Rightarrow \Delta(PV) = 0 \Rightarrow \Delta H = 0$

(b → p, r) $\Delta H = -$ve for hydrogenation and also for non-ideal solutions with negative deviation.

(c → q) For a reversible process

$dq_{(\text{Rev})\text{sys}} = -dq_{(\text{Rev})\text{surr}}$

For any process

$$dS_{\text{univ}} = dS_{\text{sys}} + dS_{\text{surr}}$$

$$= \frac{dq_{\text{sys}}}{T} + \frac{dq_{\text{surr}}}{T}$$

$$= \frac{-dq_{\text{surr}}}{T} + \frac{dq_{\text{surr}}}{T}$$

$\Rightarrow dS_{\text{univ}} = 0$

(d → r) $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$

$\Delta H_{\text{mix}} = -$ve for non-ideal solution with $-$ve deviation.

$\Delta S_{\text{mix}} = +$ve during mixture

$\Rightarrow \Delta G_{\text{mix}} = -$ve

14. (a → p) For non spontaneous process, photochemical reaction $\Delta_{\text{sys}}S > 0$.

(b → p, q) For spontaneous process, $\Delta G < 0$ or $-$ve but in photochemical reaction (non spontaneous). $\Delta G < 0$.

(c → r) At equilibrium, $\Delta S = 0$.

(d → s) For non spontaneous process, $\Delta G > 0$.

15. (a → p, r) In isothermal process ($\Delta T = 0$), $-w = q$

or $-w = 2.303RT\log\frac{V_2}{V_1}$ or $2.303RT\log\frac{P_1}{P_2}$

(b → q) Adiabatic process ($q = 0$) ($PV^{\gamma} =$ constant)

(c → q) Mathematical relationship

(d → s) $w = -P_{\text{ext}}(V_2 - V_1)$

16. (a → p, q) $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -nFE$

(b → p, r) $\Delta G^{\ominus} = -nFE^{\ominus}$ or and $\Delta G = -RT\log K$

(c → p)

(d → s) $\Delta S^{\ominus} = 2.303nR\log\left(\frac{V_2}{V_1}\right)$

17. (a → p, q; b → p, q; c → s; d → s)

18. (a → q) $\Delta H = \Delta U + \Delta nRT$, $\Delta n = n_P - n_R = 0$

$\therefore \Delta H = \Delta U$ ($n =$ number of moles)

(b → q) $\Delta H = \Delta U$ ($\because \Delta n = 0$)

(c → p) $\Delta H = \Delta U + RT$ ($\Delta n = n_P - n_R = 1$)

(d → r, s) $\Delta H = \Delta U - 2RT$ ($\Delta n = -2$)

19. (a → p, q) At equilibrium $\Delta S = 0$ and for spontaneous process

(b → q) Entropy decreases ($\Delta S < 0$) because in formation of product number of moles decrease.

(c → q, r)

(d → q, s)

20. (a → p, q; b → p, q; c → r; d → r)

21. (a → p, r) In isothermal process, $-w = 2.303RT\log\frac{V_2}{V_1}$

or $2.303RT\log\frac{P_1}{P_2}$

(b → s) In adiabatic process, $-w = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$

(c → q) In free expansion, $w = 0$

(d → q) In free expansion, $w = 0$

22. (a → q) To initial reaction, activation energy must be invested.

(b → p)

(c → r) In endothermic reaction (ΔH or $\Delta U = +$ve) heat absorbed by system.

(d → s) In exothermic reaction (ΔH or $\Delta U = -$ve) heat releases out from system to surroundings.

23. (a → q) For exothermic reaction, $\Delta H = -$ve.

(b → r) For endothermic reaction, $\Delta H = +$ve.

(c → s) For spontaneous process, $\Delta G = -$ve.

(d → p) $\Delta H = H_p - H_R$

24. (a → s) $\Delta G = \Delta H - T\Delta S$ (Gibbs–Helmholtz reaction)

(b → r)

(c → q) $\Delta H = \Delta U + P\Delta V$

(d → p)

25. (a → t)

(b → p) In adiabatic process, $q = 0$

(c → u) Isothermal process, $\Delta T = 0$

(d → q) At equilibrium, $\Delta G = 0$

(e → r) Sublimation is conversion of solid phase into gas phase.

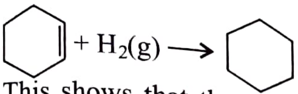
(f → s)

26. (a → p, r; b → q; c → s; d → p, r)

27. (a → r, s; b → p, r, s; c → q; d → q, r)

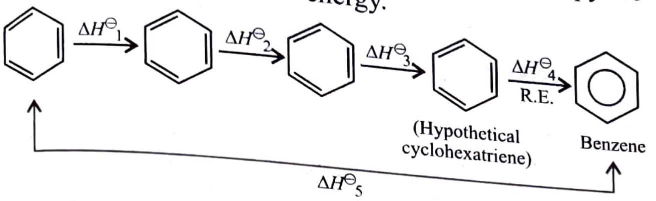
Numerical Value Type

1. (4)



$\Delta H^\ominus = -119\ \text{kJ mol}^{-1}$

This shows that the generation of one (C═C) bond in cyclohexene requires 119 kJ mol⁻¹ of enthalpy. To calculate RE resonance energy.



$\Delta H^\ominus_1 = \Delta H^\ominus_2 = \Delta H^\ominus_3 = 119\ \text{kJ mol}^{-1}$, $\Delta H^\ominus_4 = \text{RE}$

$\Delta H^\ominus_5 = \Delta_f H^\ominus(\text{benzene}) - \Delta_f H^\ominus(\text{cyclohexene})$

$= 46 - (-156) = 205\ \text{kJ mol}^{-1}$.

∴ From Hess' law:

$\Delta H^\ominus_4 = \Delta H^\ominus_5 - (\Delta H^\ominus_1 + \Delta H^\ominus_2 + \Delta H^\ominus_3)$

$= 205 - 3 \times 119 = -152\ \text{kJ mol}^{-1}$

$\therefore -38x = -152$

$x = 4$

2. (4) $\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY\ ;\ \Delta H = -100\ \text{kJ}$

Let the bond dissociation energy of X_2, Y_2, and XY be $a : \frac{a}{2} : a$ (the given ratio) kJ mol⁻¹, respectively.

$\therefore \frac{a}{2} + \frac{a}{4} - a = -100$

$\therefore a = 400$

$100x = 400$

$x = 4$

3. (5) Energy released = Energy due to formation of two single bonds

$= 2 \times 331 = 662\ \text{kJ mol}^{-1}$ of propene

ΔH polymerisation/mol $= 590 - 662 = -72\ \text{kJ mol}^{-1}$

ΔH polymerisation $= -72 \times n = -360$

$n = 5$

4. (8) $2\text{MgCl} \longrightarrow \text{Mg} + \text{MgCl}_2 \qquad \Delta H = ?$

$\text{Mg(s)} + 1/2\text{Cl}_2\text{(g)} \longrightarrow \text{MgCl} \quad \Delta H_1 = -125\ \text{kJ mol}^{-1}$

$\text{Mg(s)} + \text{Cl}_2\text{(g)} \longrightarrow \text{MgCl}_2 \quad \Delta H_2 = -642\ \text{kJ mol}^{-1}$

$\Delta H = \Delta H_2 - 2\Delta H_1 = -642 - (2 \times -125) = -392\ \text{kJ mol}^{-1}$

$\therefore -49x = -392$

$x = 8$

5. (6) $\text{KCl(s)} \longrightarrow \text{K}^\oplus\text{(g)} + \text{Cl}^\ominus\text{(g)}, \quad \Delta H_1 = 181\ \text{kcal mol}^{-1}$

$\text{KCl(s)} + \text{aq} \longrightarrow \text{K}^\oplus\text{(aq)} + \text{Cl}^\ominus\text{(aq)},$

$\Delta H_2 = 1.0\ \text{kcal mol}^{-1}$

Let the enthalpy of hydration of $\text{K}^\oplus$ is 2a kcal mol⁻¹

$\text{K}^\oplus\text{(g)} + \text{aq} \longrightarrow \text{K}^\oplus\text{(aq)}, \Delta H_3 = 2a$

$\text{Cl}^\ominus\text{(g)} + \text{aq} \longrightarrow \text{Cl}^\ominus\text{(aq)}, \qquad \Delta H_4 = a$

$\therefore \Delta H_3 = -\Delta H_1 + \Delta H_2 - \Delta H_4$

$2a = -181 + 1 - a$

$3a = -180, a = -60$

$\therefore \Delta_{\text{hyd}} H^\ominus$ of $\text{K}^\oplus = 2a = -60 \times 2 = -120$

$\therefore -20x = -120$

$x = 6$

6. (5) $\Delta_{\text{sys}} S = \frac{q_{\text{sys}}}{T_{\text{sys}}} = -\frac{300}{273 + 127}$

$= \frac{-300}{400} = \frac{-3}{4}\ \text{J K}^{-1}$

$\Delta_{\text{surr}} S = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = -\frac{300}{273 + 27}$

$= \frac{300}{300} = +1\ \text{J K}^{-1}$

$\Delta_{\text{total}} S$ or $\Delta_{\text{universe}} S = \Delta_{\text{sys}} S + \Delta_{\text{surr}} S$

$= \frac{-3}{4} + 1 = \frac{1}{4} = 0.25\ \text{J K}^{-1}$

$\therefore 0.05x = 0.25$

$x = 5$

7. (4) Entropy increases in (a), (c), (d), and (h).

8. (5) Extensive properties which depends on mass are (e), (g), (h), (i) and (j).

9. (5) Intensive properties are independent on mass. (a), (b), (c), (d) and (f).

10. (2) **Step 1. (using the third law of thermodynamics):** (For changing

$\text{H}_2\text{O(s)}\ (-10°\text{C, 1 atm}) \longrightarrow \text{H}_2\text{O(s, 0°C 1 atm)}$

$\Delta S_1 = \int_{-10}^{0} n\frac{C_P}{T}dT = 1 \times 9 \times 2.3 \times \log\frac{273}{263}$

$= 0.336\ \text{cal deg}^{-1}\ \text{mol}^{-1}$

Step 2 (using the second law of thermodynamics):

$\text{H}_2\text{O(s)}\ (0°\text{C, 1 atm}) \longrightarrow \text{H}_2\text{O(l)}(0°\text{C, 1 atm})$

$\Delta S_2 = \frac{q_{\text{rev}}}{T} = \frac{1440}{273} = 5.258\ \text{cal deg}^{-1}\ \text{mol}^{-1}$

Step 3 (using the third law of themrodynamics):

$\text{H}_2\text{O(l)}\ (0°\text{C, 1 atm}) \longrightarrow \text{H}_2\text{O(l)}(10°\text{C, 1 atm})$

$\Delta S_3 = \int_{0}^{10} n\frac{C_P}{T}dT = 1 \times 18 \times 2.3 \times \log\frac{283}{273}$

$= 0.647\ \text{cal deg}^{-1}\ \text{mol}^{-1}$

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0.336 + 5.258 + 0.647$

$= 6.258\ \text{cal deg}^{-1}\ \text{mol}^{-1}$

Archives

JEE Main

Single Correct Answer Type

1. (4)

Percentage efficiency of the fuel cell $= \dfrac{\Delta G}{\Delta H} \times 100$. The concerned reaction is

$CH_3OH(l) + 3/2O_2(g) \rightarrow CO_2(g) + 2H_2I(l)$
$\Delta G_r.\ [\Delta G_f\,(CO_2, g) + 2\Delta G_f\,H_2O, l)]$
$[-\Delta G_f\,CH_3OH, l) - 3/2\Delta G_f\,(O_2, g)]$
$= -394.4 + 2\,(-237.2) - (-166.2) - 0$
$= -394.4 - 474.4 + 166.2 = -702.6$ kJ mol^{-1}

$$\text{Percentage efficiency} = \frac{702.6}{726} \times 100$$
$$= 96.78\% \approx 97\%$$

2. (2)

Consider the heat of formation of H_2O

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$

$\Delta H = -286.20$ kJ
$\Delta H_r = \Delta H_f\,(H_2O, l) - \Delta H_f\,(H_2, g)$
$-\frac{1}{2}\Delta H_f(O_2, g) = -286.20 = \Delta H_f\,(H_2O, l) - 0 - 0$
$\Delta H_f\,(H_2O, l) = -286.20$
Now, consider the ionization of H_2O
$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$
$\Delta H = 57.32$ kJ
$\Delta H_r = \Delta H_f\,(H^+, aq) + \Delta H_f(OH^-, aq) - \Delta H_f\,(H_2O, l)$
$57.32 = 0 + \Delta H_f(OH^-, aq) - (-286.20)$
Thus, $\Delta H_f\,(OH^-, aq) = 57.32 - 286.20 = -228.80$ kJ

3. (2)

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g),\ \Delta_f H = -46\text{kJ mol}^{-1}$$

Bond enthalpy of $H_2 = 436$ kJ mol^{-1}
[+ve sign is taken because energy is supplied to break the H–H bond into its atoms]
Similarly, bond enthalpy of $N_2 = +712$ kJ mol^{-1}

$$\Delta_f H = \left[\frac{1}{2}BE(N_2) + \frac{3}{2}BE(H_2)\right] - 3BE(N-H)$$

$$-46 = \left[\frac{1}{2} \times 712 + \frac{3}{2} \times 436\right] - 3BE(N-H)$$

$-46 = (356 + 654) - 3\ BE\ (N—H)$
$3BE\ (N—H) = (1010) + 46$
$3BE\ (N—H) = 1056$
$BE\ (N—H) = 1056/3 = 352$ kJ mol^{-1}

. (2)

$\Delta G = \Delta H - T\Delta S$
Here, ΔG = Gibbs free energy
ΔH = Enthalpy change
ΔS = Entropy change
T = Temperature
As equilibrium, $\Delta G = 0$. Thus, $T\Delta S = \Delta H$, as ΔH and ΔS are +ve, for a reaction to be feasible (spontaneous), ΔG should be –ve. This can be possible only when
$T\Delta S > T_e\Delta H$, i.e., $T\Delta S > T_e\Delta S$
or $T > T_e$ [T_e = temperature at equilibrium]

. (1)

Entropy change for n moles of isothermal expansion of an ideal gas from volume V_1 to volume V_2 is

$$\Delta S = 2.303\ nR \log \frac{V_2}{V_1}$$

Hence, $n = 2$, $V_2 = 100$ dm^3, $V_1 = 10$ dm^3

$$= 2.303 \times 2 \times 8.3143 \log \frac{100}{10}$$
$$= 38.296 \text{ J mol}^{-1}\text{ K}^{-1}$$

6. (4)

$$PbO_2 + Pb \rightarrow 2PbO$$

Oxidation state +4 0 +2
Since, $\Delta G^\circ < 0$, i.e., it is negative. Therefore, the reaction is spontaneous in the forward direction. This suggest that Pb^{2+} is more stable than Pb^{4+}.

$$SnO_2 + \quad Sn \rightarrow \quad 2SnO$$

Oxidation state +4 0 +2
Since, $\Delta, G^\circ > 0$, i.e., it is positive, therefore, the reaction is non-spontaneous in the forward direction. But it will be spontaneous in the backward direction. This suggests that Sn^{2+}. These facts are also supported by the inert pair effect down the group.

7. (3)

Relation between ΔH (enthalpy change) and ΔE (internal energy change) is
$\Delta H = \Delta E + \Delta n_g RT$
where, Δn_g = (moles of gaseous products) – (moles of gaseous reactants)
For the given reaction,
$\Delta n_g = 2 - 3 = -1$
$\Rightarrow \quad -1366.5 = \Delta E - 1 \times 8.314 \times 10^{-3} \times 300$
$\therefore \quad \Delta E = -1364.0$ kJ mol^{-1}

8. (1)

$$\begin{tikzcd} \underbrace{4N_2(g) + O_2(g)} \arrow[rr, "\Delta H = -111\text{ kJ}"] \arrow[dr, "\Delta H = ?"'] & & 2N_2O_5(g) \\ & 2N_2O_5(g) \arrow[ur, "+\,54\text{ kJ}"'] & \end{tikzcd}$$

From Hess's law,
$\Delta H_f + \Delta H_{sub} = \Delta H_{reaction}$
$\Delta H_f = \Delta H_{reaction} - \Delta H_{sub}$
$= -111\text{ kJ} - (54\text{ kJ}) = -111 - 54\text{ kJ} = -165$ kJ
Thus, the enthalpy of formation, ΔH_f for $N_2O_5(s)$ is -165 kJ.

9. (3)

According to Gibbs–Helmholtz equation,
$\Delta G = \Delta H - T\Delta S$
(1) For a system, total entropy change $= \Delta S_{total}$
$\Delta H_{total} = 0$
$\therefore \quad \Delta G_{system} = -T\Delta S_{total}$

$$\therefore \quad \frac{\Delta G_{system}}{\Delta S_{total}} = -T$$

Thus, (1) is correct.
(2) For isothermal reversible process, $\Delta E = 0$
By first law of thermodynamics, $\Delta E = q + W$

$$\therefore \quad W_{reversible} = -q = -\int_{V_i}^{V_f} p\,dV$$

$$\Rightarrow \quad W_{reversible} = -nRT \ln \frac{V_f}{V_i}$$

Thus, (b) is correct.
(3) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (1)
Also, $\Delta G^\circ = -RT \ln K$

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\ln K = \frac{(\Delta H^\circ - T\Delta S^\circ)}{RT} \quad \text{[from Eq. (1)]}$$

Thus, (3) is incorrect.

(4) The standard free energy (ΔG°) is related to equilibrium constant K as

$\Delta G^\circ = -RT \ln K$

$$\therefore \quad \ln K = \frac{\Delta G^o}{RT} \Rightarrow K$$

$$= -e^{-\Delta G^o / RT}$$

Thus, (4) is also correct.

10. (1)

As the process is carrying out at constant temperature, therefore this type of expansion is called *isothermal reversible expansion*, for which, $\Delta U = 0$. Hence, $q = -W$

i.e., heat absorbed by the system is equal to the work done by the system.

Thus, $q = +\,208$ J

$W = -208$ J

11. (1)

$C_2H_5OH(l) + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(l)$

Amount of heat produced in bomb calorimeter,

$\Delta U = -1364.47\ \text{kJ mol}^{-1}$

Enthalpy of a combustion reaction is

$\Delta H = \Delta U + \Delta n_g RT$

where, ΔU = internal energy

Δn_g = moles of gas (products–reactants)

ΔR = Gas constant

T = Temperature in K

As per equation,

$\Delta n_g = 2 - 3 = -1$

$T = 25°C = 25 + 273K$

$\Rightarrow \quad T = 298$ K

$$\text{Thus, } \Delta H = -1364.47 + \left[\frac{(-1) \times 8.314 \times 298}{1000}\right]$$

$\Delta H = -1364.47 - 2.477 = -1366.947\ \text{kJ mol}^{-1}$

Hence, the enthalpy of combustion, $\Delta_C H$ for the given reaction will be $-$ 1366.947 kJ mol^{-1}.

12. (4)

$$\Delta G_r^o = \sum \Delta G_f^o\,(\text{products}) - \sum \Delta G_f^o\,(\text{reactants}) = -RT \ln K_p$$

$$2\Delta G^o_{f(NO_2)} - [2\Delta G^o_{f(NO)} + \Delta G^o_{f(O_2)}] = \Delta G_f^o = -RT \ln K_P$$

$$2\Delta G^o_{f(NO_2)} - \left[2 \times 86{,}600 + 0\right] = -RT \ln K_P$$

$$2\Delta G^o_{f(NO_2)} - 2 \times 86600 = -RT \ln K_p$$

$$2\Delta G^o_{f(NO_2)} = -RT \ln K_p + 2 \times 86600$$

$$2\Delta G^o_{f(NO_2)} = \frac{1}{2}\left[2 \times 86600 - R \times 298 \times \ln(1.6 \times 10^{12})\right]$$

$$2\Delta G^o_{f(NO_2)} = 0.5\ [2 \times 86{,}600 - R\ (298) \times \ln\ (1.6 \times 10^{12})]$$

13. (2)

$$\frac{P_o - P_s}{P_s} = \frac{n}{N}$$

$$\Rightarrow \frac{P_o - P_s}{P_s} = \frac{w_B}{M_B} \times \frac{M_A}{W_A} = \frac{185 - 183}{183} = \frac{1.2}{M_B} \times \frac{58}{100}$$

$$\Rightarrow \quad \frac{185 - 183}{183} = \frac{1.2/M}{100/58}$$

$\therefore \quad M \approx 64$ g/mol

14. (1)

$C\,(s) + O_2(g) \rightarrow CO_2(g);$ $\qquad \Delta H = -393.5$ kJ/mol

$CO(g) + \frac{1}{2}\ O_2(g) \rightarrow CO_2(g);$ $\qquad \Delta H = -283.5$ kJ/mol

$C(s) + \frac{1}{2}\ O_2(g) \rightarrow CO(g);$

$\Delta H = -393.5 + 283.5$ kJ/mol $= -110$ kJ/mol

15. (3) From First law of Thermodynamics

$\Delta U = q + \omega$

$\therefore$ for an Adiabatic process

$q = 0$

$\therefore \quad \Delta U = W$ (Adiabatic work)

16. (3) $C_{(\text{graphite})} + O_2(g) \longrightarrow CO_2(g)\ \Delta_r H^o = -393.5$ kJ/mole ...(1)

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)\ \ \Delta H_r{}^\circ = -285.8$ kJ/mole ...(2)

$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$
$\Delta H_r{}^\circ = +\ 890.3$ kJ/mole ....(3)

Eqn. 1 + 2 × eqn. 2 + eqn. 3

$-393.5 + 2\,(-285.8) + 890.3$

$= -74.8$ kJ/mole

17. (3) $C_6H_6(l) + \frac{15}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta n_g = 6 - 7.5 = -1.5$ (change in gaseous mole)

ΔU or $\Delta E = -3263.9$ kJ

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = -1.5$

$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

$T = 298$ K

So $\Delta H = -3263.9 + (-1.5)\ 8.314 \times 10^{-3} \times 298$

$= -3267.6$ kJ

ΔH = Heat at constant pressure

$\Delta U / \Delta E$ = Heat at constant volume

R = gas constant.

JEE Advanced

Single Correct Answer Type

1. **(3)** The bond energy (in kcal mol^{-1}) of a C—C single bond is approximately 100.

2. **(2)** This is possible only for elements. Chlorine is a gas at this temperature, but bromine is a liquid, so it is possible only for chlorine.

3. **(4)**

$$\begin{tikzcd} 2C(s) \arrow[d, "1410"'] & +\ H_2(g) \arrow[d, "330"] \arrow[r] & C_2H_2(g) \quad \Delta H = 225\ \text{kJ mol} \\ 2C(g) & 2H(g) \arrow[ur, "2\varepsilon_{C-H} + \varepsilon_{C\equiv C}"'] & \end{tikzcd}$$

$\therefore \quad \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{C=C} = +225$

$\therefore \quad \varepsilon_{C\equiv C} = 1740 - 700 - 225 = +815$ kJ mol.

4. **(4)** Process is isothermal reversible expansion, hence $\Delta U = 0$.

$\therefore \quad q = -W \qquad$ As $q = +208$ J $\qquad$ Hence $W = -208$ J

5. **(3)** Combustion of glucose

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

$\Delta H_{\text{combustion}} = (6 \times \Delta H_f CO_2 + 6 \times \Delta H_f H_2O) - \Delta H_f C_6H_{12}O_6$

$= (6 \times -400 + 6 \times -300) - (-1300)$

$= -2900$ kJ/mol $= -2900/180$ kJ/g $= -16.11$ kJ/g

Hence (3) is correct.

6. **(3)** $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta U = -1364.47$ kJ/mole

$\Delta H = ?$

$T = 298$ K

$\Delta n_g = (2 - 3 = -1)$

$\because \Delta H = \Delta U + \Delta n_g RT$

So, $\Delta H = -1366.95$ kJ/mole

7. (2) $H_2O(l) \longrightarrow H_2O(g)$ (100°C)

$\Delta S_{system} > 0$ $\quad \Delta S$ surrounding < 0

8. (3)

$\Delta E = q + w$

$0 = q - P_{ext}\,\Delta V$

$q = P_{ext}\,\Delta V = 3$ atm $(2 - 1)$ L $= 3$ atm L

$= (3 \times 101.3)$ Joule (1 atm L = 101.3 Joule)

$$\Delta S_{surr} = -\frac{q}{T} = \frac{-3\times 101.3}{300} = -1.013 \text{ Joule / K}$$

9. (1) $\Delta G = PdV$

$$\left[\Delta_f G^\circ_{(diamond)} = \Delta_f G^\circ_{(graphite)}\right] = PdV$$

2.9×10^3 J mol^{-1} $= P \times 2 \times 10^{-6}$ m^3 mol^{-1}

$P = 1.45 \times 10^9$ Pa

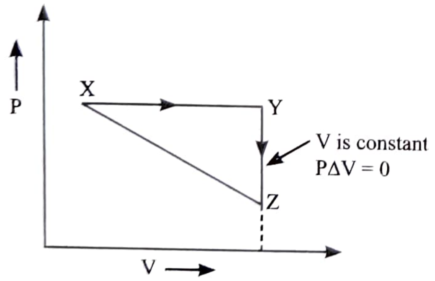
$P = 1.45 \times 10^9 \times 10^{-5}$ bar (1 Pa = 10^{-5} bar)

$P = 1.45 \times 10^4$ bar

$P = 14500$ bar

Multiple Correct Answers Type

1. (1, 3)



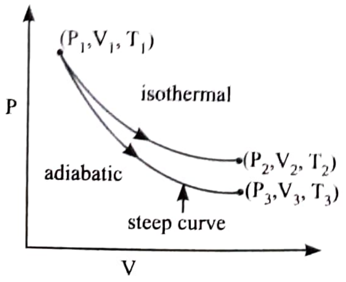
(1) $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$ (Correct) (It is state function)

(2) $W_{x\to z} = W_{x\to y} + W_{y\to z}$ (Incorrect) (Not a state function)

(3) $W_{x\to y\to z} = W_{x\to y}$ (Correct) (It is state function)

(4) $\Delta S_{x\to y\to z} = \Delta S_{x\to y}$ (Incorrect)

2. (1, 4)



(1) $T_1 = T_2$ (due to isothermal) (correct)

(2) $T_3 > T_1$ (Incorrect) cooling will take place in adiabatic expansion)

(3) $W_{isothermal} > W_{adiabatic}$ (with sign, this is incorrect) with mode it should be correct.

(4) $\Delta U_{isothermal} = 0 > \Delta U_{adiabatic} = -ve$

$|W_{isobaric}| > |W_{isothermal}| > |W_{adiabatic}|$

So, answer is (1) and (4).

3. (1, 3)

$A \rightleftharpoons P$

$(P)_{eq} > 5, (A)_{eq} < 5$

$$K_{eq} = \frac{[P]}{[A]} > 1$$

$\Delta G^0 = -RT \ln K_{eq}, \Delta G^0 < 0$

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > \frac{T_2}{T_1} > 1$$

$$\Rightarrow \frac{K_{T_1}}{K_{T_2}} > 1$$

$\Rightarrow K_{T_2} < K_{T_1}$ (exothermic)

$\Delta H^0 > 0$, since (P) at $T_2 <$ at T_1.

$T\Delta S^0 = \Delta H^0 - T\Delta S^0$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}; (\Delta H^0) > (\Delta G^0)$$

$\Delta S^0 < 0$

Also, $-T_1 \ln K_{T_1} < -T_2 \ln K_{T_2}$

$\Delta G^0{}_{T_1} < \Delta G^0{}_{T_2}$

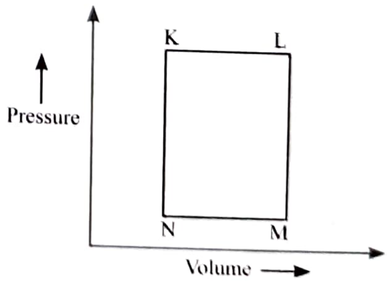
$\Delta H^0{}_{T_1} - T\Delta S^0{}_{T_2} < \Delta H^0{}_{T_2} - T\Delta S^0{}_{T_2}$

It is possible only if $\Delta S^0 < 0$.

Linked Comprehension Type

1. (3)

2. (2)



K–L heating, isobaric

L–M cooling, isochoric

M–N cooling, isobaric

N–K heating, isochoric

3. (1)

4. (2)

200 m.eq. + 100 m.eq. base → 100 m.eq. salt

$$pH = pKa + \log\frac{\text{Salt}}{\text{Acid}}$$

$$= 2 \times 10^{-5} + \log\frac{100}{100} = 5 - \log 2 = 5 - 0.3010 = 4.7$$

Matrix Match Type

1. **(a→ p, r, s)** $CO_2(s) \longrightarrow CO_2(g)$ Phase transition ΔH positive; ΔS positive

(b → r, s) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; ΔH positive; ΔH positive

(c → t) $2H^{\bullet} \longrightarrow H_2(g)$ ΔS negative

(d → p, q, t) P(white, solid) $\longrightarrow$ P(red, solid) Alltropic change and also phase transition.

- White $\xrightarrow[T\,\sim\,250°C]{\Delta}$ Red P $\Rightarrow \Delta H > 0$
- Though both red and white phosphorus are in crystalline form, but red phosphorus has a polymeric chain structure so here is decrease in entropy of the system. Thus, ΔS is negative ΔS_{white} P ~ 160 kJ and ΔS_{Red} P ~ 25 kJ

2. **(a → r, t; b → p, q, s; c → p, q, s; d → s, t)**

a. **→ (r), (t)**

$H_2O(l) \rightleftharpoons H_2O(s)$

$\Delta G = 0$ and $\Delta U = 0$, $\Delta S_{sys} < 0$

b. **→ (p), (q), (s)**

Free expansion i.e., $w = 0$, $\Delta U = 0$, $q = 0$

c. **→ (p), (q), (s)**

$q = 0$, $\Delta U = 0$, $w = 0$

d. **→ (s), (t)**

Numerical Value Type

1. **(9)** Number of moles of gas $= \frac{3.5}{28} = 0.125$

Heat evolved = Heat capacity × ΔT

$= 2.5 \times (298.45 - 298)$

$= 2.5 \times 0.45 = 1.125$ kJ

Heat evolved per mole $= \frac{1.125}{0.125} = 9$ kJ

2. **(–14.6)**

From the given data:

For $2Cu(s) + H_2O(g) \rightleftharpoons Cu_2O(s) + H_2(g)$

$\Delta G^0 = 100000$

Hence

$\Delta G^0 = 100000$

$$= -RT \ln Kp \text{ and } K_p = \frac{P_{H_2}}{P_{H_2O}} (P_{H_2O(s)} = 0.01 \text{ bar})$$

On calculating; $\ln P_{H_2} = -14.6$

1

APPENDIX

Some Useful Data and Log Tables

TABLE 1.1. Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic number	Molar mass (g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	ft	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	1	53.	126.90
Indium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)

Element	Symbol	Atomic number	Molar mass (g mol^{-1})
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93

Element	Symbol	Atomic number	Molar mass ($g\ mol^{-1}$)
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of larget known half-life.

TABLE 1.2. Specific and Molar Heat Capacities for Some Substances at 298 K and 1 Atmospheric Pressure

Substance	Specific Heat Capacity ($J\ g^{-1}$)	Molar Heat Capacity ($J\ mol^{-1}$)
Air	0.720	20.8
Water (liquid)	4.184	75.4
Ammonia (gas)	2.06	35.1
Hydrogen chloride	0.797	29.1
Hydrogen bromide	0.360	29.1
Ammonia (liquid)	4.70	79.9
Ethyl alcohol (liquid)	2.46	113.16
Ethylene glycol (liquid)	2.42	152.52
Water (solid)	2.06	37.08
Carbon tetrachloride (liquid)	0.861	132.59
Chlorofluorocarbon (CCl_2F_2)	0.5980	72.35
Ozone	0.817	39.2
Neon	1.03	20.7
Chlorine	0.477	33.8
Bromine	0.473	75.6
Iron	0.460	25.1
Copper	0.385	24.7
Aluminium	0.902	24.35
Gold	0.128	25.2
Graphite	0.720	8.65

TABLE 1.3. Molar Heat Capacities for Some Gases ($J\ mol^{-1}$)

Gas	C_P	C_V	$C_P - C_V$	C_P/C_V
Monatomic*				
helium	20.9	12.8	8.28	1.63
argon	20.8	12.5	8.33	1.66
iodine	20.9	12.6	8.37	1.66
mercury	20.8	12.5	8.33	1.66
Diatomic**				
hydrogen	28.6	20.2	8.33	1.41
oxygen	29.1	20.8	8.33	1.39
nitrogen	29.0	20.7	8.30	1.40
hydrogen chloride	29.6	21.0	8.60	1.39
carbon monoxide	29.0	21.0	8.00	1.41
Triatomic**				
nitrous oxide	39.0	30.5	8.50	1.28
carbon dioxide	37.5	29.0	8.50	1.29
Polyatomic**				
ethane	53.2	44.6	8.60	1.19

* Translational kinetic energy only.

** Translational, vibrational, and rotational energy.

TABLE 1.4. Physical Constants

Quantity	Symbol Traditional	Units	SI Units
Acceleration of gravity	g	980.6 cm s^{-1}	9.806 m s^{-1}
Atomic mass unit (1/12 the mass of ^{12}C atom)	amu or u	1.6606×10^{-24} g	1.6606×10^{-27} kg
Avogadro constant	N_A	6.022×10^{23} particles mol^{-1}	6.022×10^{23} particles mol^{-1}
Bohr radius	a_0	0.52918 Å 5.2918×10^{-9} cm	5.2918×10^{-11} m
Boltzmann constant	k	1.3807×10^{-16} erg K^{-1}	1.3807×10^{-23} J K^{-1}
Charge-to-mass ratio of electron	e/m	1.7588×10^{8} C g^{-1}	1.7588×10^{11} C kg^{-1}
Electronic charge	e	1.60219×10^{-19} C 4.8033×10^{-19} esu	1.60219×10^{-19} C
Electron rest mass	m_e	9.10952×10^{-28} g 0.00054859 u	9.10952×10^{-31} kg
Faraday constant	F	96,487 C eq^{-1} 23.06 kcal $(V\ eq)^{-1}$	96,487 C $(mol\ e^-)^{-1}$ 96,487 J $(V.eq\ mol\ e^-)^{-1}$
Gas constant	R	0.8206 L atm $(mol\ K)^{-1}$ 1.8206 L atm $(mol\ K)^{-1}$	8.3145 kPa dm^3 $(mol\ K)^{-1}$ 8.3145 J $(mol\ K)^{-1}$
Molar volume (STP)	V_m	22.710981 L mol^{-1} 22.710981 dm^3 mol^{-1}	22.710981×10^{-3} m^3 mol^{-1}
Neutron rest mass	m_n 1.008665 u	1.67495×10^{-24} g	1.67495×10^{-27} kg
Planck constant	h	6.6262×10^{-27} ergs	6.6262×10^{-34} J s
Proton rest mass	m_p 1.007277 u	1.6726×10^{-24} g	1.6726×10^{-27} kg
Rydberg constant	R_∞ 2.1799×10^{-11} erg	3.289×10^{15} cycles s^{-1} 2.1799×10^{-18} J	1.0974×10^{7} m^{-1}
Speed of light (in a vacuum)	c (186,281 miles s^{-1})	2.9979×10^{10} cm s^{-1}	2.9979×10^{8} m s^{-1}

$\pi = 3.1416$ $\quad 2.303R = 4.576$ cal $(mol\ K)^{-1} = 19.15$ J $(mol\ K)^{-1}$

$e = 2.71828$ $\quad 2.303RT$ (at 25°C) $= 1364$ cal $mol^{-1} = 5709$ J mol^{-1}

$\ln X = 2.303 \log X$

TABLE 1.5. Some Useful Conversion Factors

Common Unit of Mass and Weight

1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram

1 kilogram = 1000 grams = 2.205 pounds

1 gram = 10 decigrams = 100 centigrams

= 1000 milligrams

1 gram = 6.022×10^{23} atomic mass units or u

1 atomic mass unit = 1.6606×10^{-24} gram

1 metric tonne = 1000 kilograms = 2205 pounds

Common Unit of Volume

1 quart = 0.9463 litre

1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre

1 millilitre = 1 cubic centimetre

= 0.001 litre

= 1.056×10^{-3} quart

1 cubic foot = 28.316 litres = 29.902 quarts

= 7.475 gallons

Common Units of Energy

1 joule = 1×10^{7} ergs

1 thermochemical calorie*

= 4.184 joules

= 4.184×10^{7}ergs

= 4.129×10^{-2} litre-atmospheres

= 2.612×10^{19} electron volts

1 ergs = 1×10^{-7} joule = 2.3901×10^{-8} calorie

1 electron volt = 1.6022×10^{-19} joule

= 1.6022×10^{-12}erg = 95.487 kJ mol^{-1}**

1 litre-atmosphere = 24.217 calories

= 101.32 joules = 1.0132×10^{9} ergs

1 British thermal unit = 1055.06 joules

= 1.05506×10^{10} ergs = 252.2 calories

Common Units of Length

1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres

1 yard = 36 inches = 0.9144 metre

1 metre = 100 centimetres

= 39.37 inches

= 3.281 feet = 1.094 yards

1 kilometre = 1000 metres = 1094 yards = 0.6215 mile

1 Angstrom = 1.0×10^{-8} centimetre

= 0.10 nanometre

= 1.0×10^{-10} metre

= 3.937×10^{-9} inch

Common Units of Force† and Pressure

1 atmosphere = 760 millimetres of mercury

= 1.013×10^{5} pascals

= 14.70 pounds per square inch

1 bar = 10^{5} pascals

1 torr = 1 millimetre of mercury

1 pascal = 1 kg ms^{-2} = 1 N m^{-2}

Temperature

SI base unit: Kelvin (K)

K = –273.15°C

K = °C + 273.15

°F = 1.8(°C) + 32

$$°C = \frac{°F - 32}{1.8}$$

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*The amount of heat required to raise the temperature of one gram of water from 14.5°C to 15.5°C.

**The other units are per particle and must be multiplied by 6.022×10^{23} to be strictly comparable.

†Force: 1 newton (N) = 1 kg m s^{-2}, i.e., the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second.

TABLE 1.6. Thermodynamics Data at 298 K

INORGANIC SUBSTANCES

Substance	Enthalpy of formation $\Delta_f H^{\ominus}$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^{\ominus}$ (kJ mol^{-1})	Entropy* $S^{\ominus}$ (J K mol^{-1})
Aluminium			
$Al(s)$	0	0	28.33
$Al^{3+}(aq)$	–524.7	–481.2	–321.7
$Al_2O_3(s)$	–1675.7	–1582.3	50.92
$Al(OH)_3(s)$	–1276	—	—
$AlCl_3(s)$	–704.2	–628.8	110.67
Antimony			
$SbH_3(g)$	145.11	147.75	232.78
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
Arsenic			
$As(s)$, gray	0	0	35.1
$As_2S_3(s)$	–169.0	–168.6	163.6
$AsO_4^{3-}(aq)$	–888.14	–648.41	–162.8
Barium			
$Ba(s)$	0	0	62.8
$Ba^{2+}(aq)$	–537.64	–560.77	9.6
$BaO(s)$	–553.5	–525.1	70.42
$BaCO_3(s)$	–1216.3	–1137.6	112.1
$BaCO_3(aq)$	–1214.78	–1088.59	–47.3
Boron			
$B(s)$	0	0	5.86
$B_2O_3(s)$	–1272.8	–1193.7	53.97
$BF_3(g)$	–1137.0	–1120.3	254.12
Bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.11	245.46
$Br(g)$	111.88	82.40	175.02
$Br^{\ominus}(aq)$	–121.55	–103.96	82.4
$HBr(g)$	–36.40	–53.45	198.70
$BrF_3(g)$	–255.60	–229.43	292.53
Calcium			
$Ca(s)$	0	0	41.42
$Ca(g)$	178.2	144.3	154.88
$Ca^{2+}(aq)$	–542.83	–553.58	–53.1
$CaO(s)$	–635.09	–604.03	39.75
$Ca(OH)_2(s)$	–986.09	–898.49	83.39
$Ca(OH)_2(aq)$	–1002.82	–868.07	–74.5
$CaCO_3(s)$, calcite	–1206.92	–1128.8	92.9
$CaCO_3(s)$, aragonite	–1207.1	–1127.8	88.7

Substance	Enthalpy of formation $\Delta_f H^\ominus$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^\ominus$ (kJ mol^{-1})	Entropy* $S^\ominus$ (J K mol^{-1})
$CaCO_3$(aq)	–1219.97	–1081.39	–110.0
CaF_2(s)	–1219.6	–1167.3	68.87
CaF_2(aq)	–1208.09	–1111.15	–80.8
$CaCl_2$(s)	–795.8	–748.1	104.6
$CaCl_2$ {aq)	–877.1	–816.0	59.8
$CaBr_2$(s)	–682.8	–663.6	130
CaC_2(s)	–59.8	–64.9	69.96
CaS(s)	–482.4	–477.4	56.5
$CaSO_4$(s)	–1434.11	–1321.79	106.7
$CaSO_4$(aq)	–1452.10	–1298.10	–33.1
Carbon[†]			
C(s), graphite	0	0	5.740
C(s), diamond	1.895	2.900	2.377
C(g)	716.68	671.26	158.10
CO(g)	–110.53	–137.17	197.67
CO_2g)	–393.51	–394.36	213.74
CO_3^{2-}(aq)	–677.14	–527.81	–56.9
CCl_4(l)	–135.44	–65.21	216.40
CS_2(l)	89.70	65.27	151.34
HCN(g)	135.1	124.7	201.78
HCN(l)	108.87	124.97	112.84
Cerium			
Ce(s)	0	0	72.0
Ce^{3+}(aq)	–696.2	–672.0	–205.0
Ce^{4+}(aq)	–537.2	–503.8	–301.0
Chlorine			
Cl_2(g)	0	0	223.07
Cl(g)	121.68	105.68	165.20
$Cl^\ominus$(aq)	–167.16	–131.23	56.5
HCl(g)	–92.31	–95.30	186.91
HCl(aq)	–167.16	–131.23	56.5
Copper			
Cu(s)	0	0	33.15
$Cu^\oplus$(aq)	71.67	49.98	40.6
Cu^{2+}(aq)	64.77	65.49	–99.6
Cu_2O(aq)	–168.6	–146.0	93.14
CuO(s)	–157.3	–129.7	42.63
$CuSO_4$(s)	–771.36	–661.8	109
$CuSO_4 \cdot 5H_2O$(s)	–2279.7	–1879.7	300.4

[†] Separate table has been provided for organic compounds under the same appendix.

Substance	Enthalpy of formation $\Delta_f H^\ominus$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^\ominus$ (kJ mol^{-1})	Entropy* $S^\ominus$ (J K mol^{-1})
Mercury			
$Hg(l)$	0	0	76.02
$Hg(g)$	61.32	31.82	174.96
$HgO(s)$	–90.83	–58.54	70.29
$Hg_2Cl_2(s)$	–265.22	–210.75	192.5
Nitrogen			
$N_2(g)$	0	0	191.61
$NO(g)$	90.25	86.55	210.76
$N_2O(g)$	82.05	104.20	219.85
$NO_2(g)$	33.18	51.31	240.06
$N_2O_4(g)$	9.16	97.89	304.29
$HNO_3(l)$	–174.10	–80.71	155.60
$HNO_3(aq)$	–207.36	–111.25	146.4
$NO_3^{\ominus}(aq)$	–205.0	–108.74	146.4
$NH_3(g)$	–46.11	–16.45	192.45
$NH_3(aq)$	–80.29	–26.50	111.3
$NH_4^{\oplus}$ (aq)	–132.51	–79.31	113.4
$NH_2OH(s)$	–114.2	—	—
$HN_3(g)$	294.1	328.1	238.97
$N_2H_4(l)$	50.63	149.34	121.21
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4ClO_4(s)$	–295.31	–88.75.	186.2
Oxygen			
$O_2(g)$	0	0	205.14
$O_3(g)$	142.7	163.2	238.93
$OH^{\ominus}(aq)$	–229.99	–157.24	–10.75
Phosphorus			
P(s), white	0	0	41.09
$P_4(g)$	58.91	24.44	279.98
$PH_3(g)$	5.4	13.4	210.23
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$H_3PO_3(aq)$	–964.8	—	—
$H_3PO_4(l)$	–1266.9	—	—
$H_3PO_4(aq)$	–1277.4	–1018.7	—
$PCl_3(l)$	–319.7	–272.3	217.18
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.6
Potassium			
$K(s)$	0	0	64.18
$K(g)$	89.24	60.59	160.34
$K^{\oplus}(aq)$	–252.38	–283.27	102.5
$KOH(s)$	–424.76	–379.08	78.9

Substance	Enthalpy of formation $\Delta_f H^{\ominus}$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^{\ominus}$ (kJ mol^{-1})	Entropy* $S^{\ominus}$ (J K mol^{-1})
KOH(aq)	–482.37	–440.50	91.6
KF(s)	–567.27	–537.75	66.57
KCl(s)	–436.75	–409.14	82.59
KBr(s)	–393.80	–380.66	95.90
KI(s)	–327.90	–324.89	106.32
$KClO_3$(s)	–397.73	–296.25	143.1
$KClO_4$(s)	–432.75	–303.09	151.0
K_2S(s)	–380.7	–364.0	105
K_2S(aq)	–471.5	–480.7	190.4
Silicon			
Si(s)	0	0	18.83
SiO_2(s)	–910.94	–856.64	41.84
Silver			
Ag(s)	0	0	42.55
$Ag^{\oplus}$(aq)	105.58	77.11	72.68
Ag_2O(s)	–31.05	–11.20	121.3
AgBr(s)	–100.37	–96.90	107.1
AgBr(aq)	–15.98	–26.86	155.2
AgCl(s)	–127.07	–109.79	96.2
AgCl(aq)	–61.58	–54.12	129.3
AgI(s)	–61.84	–66.19	115.5
AgI(aq)	50.38	25.52	184.1
$AgNO_3$(s)	–124.39	–33.41	140.92
Sodium			
Na(s)	0	0	51.21
Na(g)	107.32	76.76	153.71
$Na^{\oplus}$(aq)	–240.12	–261.91	59.0
NaOH(s)	–425.61	–379.49	64.46
NaOH(aq)	–470.11	419.15	48.1
NaCl(s)	–411.15	–384.14	72.13
NaCl(aq)	–407.3	–393.1	115.5
NaBr(s)	–361.06	–348.98	86.82
NaI(s)	–287.78	–286.06	98.53
$NaHCO_3$(s)	–947.7	–851.9	102.1
Na_2CO_3(s)	–1130.9	–1047.7	136.0
Sulphur			
S(s), rhombic	0	0	31.80
S(s), moniclinic	0.33	0.1	32.6
S^{2-} (aq)	33.1	85.8	–14.6
SO_2(g)	–296.83	–300.19	248.22
SO_3(g)	–395.72	–371.06	256.76
H_2SO_4(I)	–813.99	–690.00	156.90
H_2SO_4(aq)	–909.27	–744.53	20.1

Substance	Enthalpy of formation $\Delta_f H^\ominus$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^\ominus$ (kJ mol^{-1})	Entropy* $S^\ominus$ (J K mol^{-1})
SO_4^{2-}(aq)	–909.27	–744.53	20.1
H_2S(g)	–20.63	–33.56	205.79
H_2S(aq)	–39.7	–27.83	121
SF_6(g)	–1209	–1105.3	291.82
Tin			
Sn(s), white	0	0	51.55
Sn(s), gray	–2.09	0.13	44.14
SnO(s)	–285.8	–256.9	56.5
SnO_2(s)	–580.7	–519.6	52.3
Zinc			
Zn(s)	0	0	41.63
Zn^{2+}(aq)	–153.89	–147.06	–112.1
ZnO(s)	–348.28	–318.30	43.64
Zn(g)	+130.73	+95.14	160.93

ORGANIC SUBSTANCES

Substance	Enthalpy of combustion $\Delta_{comb}H^\ominus$ (kJ mol^{-1})	Enthalpy of formation $\Delta_f H^\ominus$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^\ominus$ (kJ mol^{-1})	Entropy* $S^\ominus$ (J K mol^{-1})
Hydrocarbons				
CH_4(g), methane	–890	–74.81	–50.72	186.26
C_2H_2(g), ethyne (acetylene)	–1300	226.73	209.20	200.94
C_2H_4(g), ethene (ethylene)	–1411	52.26	68.15	219.56
C_2H_6(g), ethane	–1560	–84.68	–32.82	229.60
C_3H_6(g), propene (propylene)	–2058	20.42	62.78	266.6
C_3H_6(g), cyclopropane	–2091	53.30	104.45	237.4
C_3H_8(g), propane	–2220	–103.85	–23.49	270.2
C_4H_{10}(g), butane	–2878	–126.15	–17.03	310.1
C_5H_{12}(g), pentane	–3537	–146.44	–8.20	349
C_6H_6(l), benzene	–3268	49.0	124.3	173.3
C_6H_6(g)	–3302	—	—	—
C_7H_8(l), toluene	–3910	12.0	113.8	221.0
C_7H_8(g)	–3953	—	—	—
C_6H_{12}(l), cyclohexane	–3920	–156.4	26.7	204.4
C_6H_{12}(g),	–3953	—	—	—
C_8H_{18}(1), octane	–5471	–249.9	6.4	358
Alcohols and phends				
CH_3OH(l), methanol	–726	–238.86	–166.27	126.8
CH_3OH(g),	–764	–200.66	–161.96	239.81
C_2H_5OH(1), ethanol	–1368	–277.69	–174.78	160.7
C_2H_5OH(g)	–1409	–235.10	–168.49	282.70
C_6H_5OH(s), phenol	–3054	–164.6	–50.42	144.0

Substance	Enthalpy of combustion $\Delta_{comb}H^\ominus$ (kJ mol^{-1})	Enthalpy of formation $\Delta_f H^\ominus$ (kJ mol^{-1})	Gibbs energy of formation $\Delta_f G^\ominus$ (kJ mol^{-1})	Entropy* $S^\ominus$ (J K mol^{-1})
Carboxylic acid				
HCOOH(l), formic acid	−255	−124.72	−361.35	128.95
CH_3COOH(l), acetic acid	−875	−484.5	−389.9	159.8
CH_3COOH(aq)	—	−185.76	−396.64	86.6
$(COOH)_2$(s), oxalic acid	−254	−827.2	−697.9	120
C_6H_5COOH(s), benzoic acid	−3227	−385.1	−245.3	167.6
Aldehydes and ketones				
HCHO(g), methanal (formaldehyde)	−571	−108.57	−102.53	218.77
CH_3CHO(l), ethanal (acetaldehyde)	−1166	−192.30	−128.12	160.2
CH_3CHO(g)	−1192	−166.19	−128.86	250.3
CH_3COCH_3(l), propanone (acetone)	−1790	−248.1	−155.4	200
Sugars				
$C_6H_{12}O_6$(s), glucose	−2808	−1268	−910	212
$C_6H_{12}O_6$(aq)	—	—	−917	—
$C_6H_{12}O_6$(s), fructose	−2810	−1266	—	—
$C_{12}H_{22}O_{11}$(s), sucrose	−5645	−2222	−1545	360
Nitrogen compounds				
$CO(NH_2)_2$(s), urea	−632	−333.51	−197.33	104.60
$C_6H_5NH_2$(1), aniline	−3393	31.6	149.1	191.3
NH_2CH_2COOH(s), glycine	−969	−532.9	−373.4	103.51
CH_3NH_2(g), methylamine	−1085	−22.97	32.16	243.41

*The entropies of individual ions in solution are determined by getting the entropy of $H^\oplus$ in water equal to zero and then defining the entropies of all other ions relative to this value. Hence, a negative entropy is one that is lower than the entropy of $H^\oplus$ in water.

Note:

It may be noted that:

- **a.** Standard enthalpy of formation of the substance is also called its standard enthalpy and can also be denoted as $H^\ominus$.
- **b.** By convention, standard enthalpy for formation, $\Delta_f H^\ominus$, of an element in reference state, i.e., its most stable state of aggregation, is taken as zero.
- **c.** Standard state of elements refers to the pure element in its most stable form at 298 K and 1 bar pressure. For example, the standard state of carbon, sulphur, oxygen, mercury, bromine, and iodine are C(graphite), S_8(rhombic), O_2(g), Br_2(l), and I_2(s), respectively.

Chapter 7

Concept Application Exercises

Exercise 7.1

Objective Type

1. (2) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
According the to of law mass action,
$K_c = [CO_2]$, because the concentration of solid substance is taken as unity.

2. (4) As $K_p = \dfrac{(P_{CO})^2}{P_{CO_2}} = \dfrac{(4)^2}{2} = \dfrac{16}{2} = 8$

3. (2)

4. (1) Because higher the value of equilibrium constant more favourable would be the product formation.

5. (3) **6. (3)**

7. (3) as $\Delta n = 0$

$\therefore K_p = K_c(RT)^0$

$\therefore K_p = K_c$

8. (1)

9. (1) $K = \dfrac{[NH_3]^2}{[H_2]^3\,[N_2]}$ for 50% N_2

$K = \dfrac{4}{27}$

10. (1)

$$\begin{array}{lcccc} & H_2(g) & + \; CO_2(g) & \rightleftharpoons \; CO(g) & + \; H_2O(g) \\ t=0 & x & x & 0 & 0 \\ t=t_{Eq} & 1-x & 1-x & x & x \end{array}$$

$$\therefore K = \frac{[CO][H_2O]}{[H_2][CO_2]} = \frac{x^2}{(1-x)^2}$$

11. (1) $2Ag_2O(s) \rightleftharpoons 4Ag(s) + O_2(g)$

$\therefore K_p = P_{O2}$

12. (2)

$$\begin{array}{lccc} & PCl_5(g) \rightleftharpoons & PCl_3(g) & + \; Cl_2(g) \\ t=0 & 2 & 0 & 0 \\ t=t_{eq} & \dfrac{2-0.08}{2} & \dfrac{0.8}{2} & \dfrac{0.8}{2} \end{array}$$

$$\therefore K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{0.8}{2} \times \frac{0.8}{2}}{\frac{1.2}{2}} = \frac{0.64}{2.4} = 0.266$$

13. (1) As $K_p = K_c(RT)^{\Delta n}$

$\Delta n = 3 - 2 = 1$

$\therefore K_p = K_c(RT)^{\Delta n}$

or $K_p > K_c$

14. (1) $P_{NH_3}{:}P_{CO_2} = 2{:}1$

$\therefore P_{NH_3} = 2$ atm; $P_{CO_2} = 1$ atm

$K^{`}_p = (P_{NH_3})^2\,(P_{CO_2}) = 2^2 \times 1 = 4$

15. (4)

$$\begin{array}{lcccc} & A & + \; B & \rightleftharpoons \; C & + \; D \\ t=0 & a & a & 0 & 0 \\ t_{Eq} & a-x & a-x & x & x \end{array}$$

Given that concentration of D is twice of A.

$$\therefore \quad x = 2(a-x) \text{ or } (a-x) = \frac{x}{2}$$

$$K = \frac{x \times x}{(a-x)\,(a-x)} = \frac{x \times x}{\frac{x}{2} \times \frac{x}{2}} = 4$$

16. (1)

$$\begin{array}{lccc} & H_2 & + \; I_2 & \rightleftharpoons \; 2HI \\ t=0 & 15 & 5.2 & 0 \\ t_{Eq} & 15-5 & 5.2-5 & 10 \end{array}$$

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{100}{10 \times 0.2} = 50$$

17. (2) As $K_p = K_c(RT)^{\Delta n}$

$\Delta n = 3 - 2 = 1$

$\therefore K_p = K_c(RT)$

18. (4) **19. (4)**

20. (1) $K_p = K_c(RT)^{\Delta n}$

$\Delta n = 1 - 2 = -1$

$\therefore K_p = K_c(RT)^{-1}$

or $\dfrac{K_p}{K_c} = \dfrac{1}{RT}$

21. (2)

22. (4) $K_p = K_c(RT)^{\Delta n}$

$$\Delta n = 1 - \left(1 + \frac{1}{2}\right) = \frac{1}{2}$$

$$\therefore \frac{K_p}{K_c} = \frac{1}{\sqrt{RT}}$$

23. (1) $K_c = \dfrac{[C]}{[A][B]} = \text{mol}^{-1}\text{L}$

24. (4)

25. (2)

26. (3) We know, $K = \dfrac{K_f}{K_b} = \dfrac{1 \times 10^{-4}}{2.5 \times 10^{-2}} = 4 \times 10^{-3}$

27. (3) When the equation is reversed, the equilibrium constant for the reaction is reciprocal of K for the forward reaction.

$$K_2 = \frac{1}{K_1} = \frac{1}{20} = 5 \times 10^{-2} \text{ or } 0.05$$

28.

$$\begin{array}{ccccc} 2KCN & + \; AgNO & \rightleftharpoons \; Ag(CN)_2^- & + \; KNO_3 & + \; K^{\oplus} \\ 0.1 & 0.03 & 0 & 0 & 0 \\ (0.1-0.06) & 0 & 0.03 & 0.03 & 0.03 \end{array}$$

$\therefore\ [\mathrm{Ag(CN)_2^-}] = 0.03\ \mathrm{M}$

Now use

$$\begin{array}{ccccc} \mathrm{Ag(CN)_2^{\ominus}} & \rightleftharpoons & \mathrm{Ag^{\oplus}} & + & \mathrm{2CN^{\ominus}} \\ 0.03 & & 0 & & 0.04 \\ (0.03-a) & & a & & 0.04+a \end{array}$$

Since K_c is too small and dissociation of $\mathrm{Ag(CN)_2^{\ominus}}$ less, thus

$\therefore\ 0.04 + a \approx 0.04$ and $0.03 - a \approx 0.03$

$\therefore\ [\mathrm{Ag(CN)_2^{\ominus}}] = 0.03;\ [\mathrm{Ag^{\oplus}}] = a;\ [\mathrm{CN^{\ominus}}] = 0.04$

$$\text{Now, } K_c = \frac{[\mathrm{Ag^{\oplus}}][\mathrm{CN^{\ominus}}]^2}{[\mathrm{Ag(CN)_2^{\ominus}}]} = \frac{a \times (0.04)^2}{0.03}$$

$\therefore\ a = 7.5 \times 10^{-18}$

29. (3)

$$\begin{array}{cccccccl} \mathrm{SO_2(g)} & + & \mathrm{NO_2(g)} & \rightleftharpoons & \mathrm{SO_3(g)} & + & \mathrm{NO(g)} & \\ 1 & & 1 & & 1 & & 1 & \text{Intital conc} \\ 1-x & & 1-x & & 1+x & & 1+x & \text{At Eq.} \end{array}$$

$$K = \frac{[\mathrm{SO_3}][\mathrm{NO}]}{[\mathrm{SO_2}][\mathrm{NO_2}]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4 \text{ or } x = 0.6$$

$[\mathrm{NO_2}] = 1 - x = 1 - 0.6 = 0.4\ \mathrm{mol\ L^{-1}}$

30.

$$\begin{array}{ccccc} \mathrm{2HI} & \longrightarrow & \mathrm{H_2} & + & \mathrm{I_2} \\ 1 & & 0 & & 0 \\ 1-x & & \frac{x}{2} & & \frac{x}{2} \\ 1-0.22=0.78 & & 0.11 & & 0.11 \end{array}$$

$$x = 22\% \text{ of } 1 \text{ mol} = \frac{22}{100} \times 1 = 0.22$$

$$K = \frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]} = \frac{0.11 \times 0.11}{(0.78)^2} = 0.0199$$

$\therefore$ (b)

31. (1)

$$\begin{array}{cccccc} & \mathrm{AB(g)} & \rightleftharpoons & \mathrm{A(g)} & + & \mathrm{B(g)} \\ t=0 \text{ (moles)} & a & & 0 & & 0 \\ t=t_{\text{eq}} & a-x & & x & & x \end{array}$$

$$\Rightarrow K_p = \frac{p_A \cdot p_B}{p_{AB}} = \frac{\left(\frac{x}{a+x}P\right)\left(\frac{x}{a+x}\cdot P\right)}{\left(\frac{a-x}{a+x}\cdot P\right)}$$

$$\Rightarrow K_p = \frac{x^2 P}{a^2 - x^2} \text{ and } \alpha = \frac{x}{a} = \frac{1}{3} \Rightarrow P = 8\,K_p$$

32. (4) K_{eq} depends only on T

33. (4)

$$\begin{array}{cccccc} & \mathrm{AB(g)} & \rightleftharpoons & \mathrm{A(g)} & + & \mathrm{B(g)} \\ t=0 \text{ (moles)} & 1 & & 0 & & 0 \\ t=t_{\text{eq}} & 1-\alpha & & \alpha & & \alpha \end{array}$$

$$\Rightarrow K_p = \frac{p_A \cdot p_B}{p_{AB}} = \frac{\left(\frac{\alpha}{a+\alpha}\cdot P\right)\left(\frac{\alpha}{a+\alpha}\cdot P\right)}{\frac{1-\alpha}{1+\alpha}\cdot P}$$

$$\Rightarrow K_p = \frac{x^2 P}{1-\alpha^2} = 4P \text{ (given)} \Rightarrow \alpha = 0.9$$

Exercise 7.2

Objective Type

1. **(1)**
2. **(4)** Because the reaction is exothermic and on product side the number of moles of substance is less.
3. **(4)**
4. **(1)** As $\Delta n = 0$.
5. **(1)**
6. **(2)** Liberation of $\mathrm{CO_2(g)}$ shifts the reaction on forward direction.
7. **(3)** Number of moles are less on reactant side, hence on lowering the pressure, reaction will proceed in forward direction.

8. (2) 9. (3) 10. (1) **11. (1)** **15. (3)**

12. (1) 13. (4) **14. (2)**

16. (1) Ist Method:

Using direct relation, we get

$$\frac{K_{p_1}}{K_{p_2}} = \frac{1}{9} = \frac{(2)^2 P_1}{P_2}$$

$$\therefore\ \frac{P_1}{P_2} = \frac{1}{36}$$

2nd Method:

$$\begin{array}{lccc} \text{Soln. for} & X & \rightleftharpoons & 2Y \\ \text{Initial moles} & 1 & & 0 \\ \text{Eq. mol} & 1-x & & 2x \end{array}$$

Total mol $= 1 - x + 2x = 1 + x$

$$p_x = \left(\frac{1-x}{1+x}\right)P_1 \qquad p_y = \left(\frac{2x}{1+x}\right)P_1.$$

$$K_{p1} = \frac{(p_y)^2}{p_x} = \frac{\left[\left(\frac{2x}{1+x}\right)P_1\right]^2}{\left(\frac{1-x}{1+x}\right)P_1}$$

$$= \frac{4x^2 P_1}{(1-x^2)}$$

$$\begin{array}{lccccc} \text{Similarly for} & Z & \rightleftharpoons & P & + & Q \\ \text{Initial mol} & 1 & & 0 & & 0 \\ \text{Equilibrium mol} & 1-x & & x & & x \end{array}$$

Total mol: $1 - x + x + x = 1 + x$.

$$p_z = \left(\frac{1-x}{1+x}\right)P_2, \quad p_Q\left(\frac{x}{1+x}\right)P_2, \quad p_P = \left(\frac{x}{1+x}\right)P_2$$

$$k_{p2} = \frac{p_P \times p_Q}{p_z} = \frac{\left(\frac{x}{1+x}\right)P_2 \times \left(\frac{x}{1+x}\right)P_2}{\left(\frac{1-x}{1+x}\right)P_2}$$

$$= \frac{x^2 P_2}{(1-x^2)}$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{4\cancel{x^2}P_1}{(1-\cancel{x^2})} \times \frac{(1-\cancel{x^2})}{\cancel{x^2}\,P_2} = \frac{4P_1}{P_2}$$

$K_{p_1} : K_{p_2} = 1 : 9$ (Given)

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{4P_1}{P_2}$$

$$\frac{1}{9} = \frac{4P_1}{P_2}$$

$$\therefore \frac{P_1}{P_2} = \frac{1}{36}.$$

or $P_1 : P_2 = 1 : 36$.

17. (2) $N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 4$

From graph, at point A, Q = 0

When $[N_2O_4] = [NO_2] = 0.1$ M

$$\Rightarrow Q = \frac{[NO_2]^2}{[N_2O_4]} = 0.1 < K_c \Rightarrow \text{Reaction is moving in}$$

forward direction.

At point D or F, $[NO_2]$ and $[N_2O_4]$ is constant with time $\Rightarrow$ Achievement of chemical equilibrium.

18. (3)

	$P_4(g)$	+ $6Cl_2(g)$	$\rightleftharpoons 4PCl_3(g)$
$t = 0$ (moles)	a	a	0
$t = t_{eq}$	$a - x$	$a - 6x$	$4x$

$$[Cl_2] = \frac{a-6x}{V};\ [PCl_3] = \frac{4x}{V};\ [P_4] = \frac{a-x}{V}$$

Clearly, $[Cl_2] < [P_4]$

Exercises

Single Correct Answer Type

1. (4)

	PCl_5	$\rightleftharpoons PCl_3$	+ Cl_2
Initial	1	0	0
Final	$1-\alpha$	α	α
Partial pressure	$= \frac{1-\alpha}{1+\alpha}.P$	$\frac{\alpha}{1+\alpha}.P$	$\frac{\alpha}{1+\alpha}.P$

Total mole $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$K_p = \frac{\frac{\alpha}{1+\alpha}P.\frac{\alpha}{1+\alpha}.P}{\frac{1-\alpha}{1+\alpha}P} = \frac{\alpha^2 P}{1-\alpha^2}$$

2. (4) Since the number of moles decreases. So reaction is favoured forward by increasing pressure,

$$\Delta n = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$$

3. (2) Since K increases on increasing temperature, so the reaction will go forward by increasing temperature and hence is endothermic.

4. (3)

5. (2) $\qquad A + 2B \rightleftharpoons 2C, \qquad$ ...(i) $K = 40$

and for $\qquad C \rightleftharpoons B + \frac{1}{2}A, \qquad$ ...(i) $K_1 = ?$

$$K = \frac{1}{\sqrt{K}} = \frac{1}{(40)^{1/2}}$$

Since equation (2) is obtained by reversing and dividing by 2, the equation (1).

6. (3) Since there is no effect on the equilibrium by adding inert gas at constant volume.

7. (1) With the increase of temperature, k value decreases, so the forward reaction decreases with increase of temperature. This implies that reaction will proceed in forward direction with decrease of temperature, i.e., heat is liberated and hence forward reaction is exothermic.

8. (3)

	N_2O_4	$\rightleftharpoons 2NO_2$
Initial	1	0
Final	$1-x$	$2x$

$1 - x = 0.2$ mol $\qquad 2x = 2 \times 10^{-3}$ mol

$$[N_2O_4] = \frac{0.2}{2} = 0.1 \text{ M} \qquad [NO_2] = \frac{2\times10^{-3}}{2} = 10^{-3}\text{M}$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(10^{-3})^2}{0.1} = 10^{-5}$$

9. (3)

	N_2O_4	$\rightleftharpoons 2NO_2$
Initial	1	0
Final	$1-\alpha$	2α

[Total moles $= 1 - \alpha + 2\alpha = 1 + \alpha$]

Partial pressure $\qquad \frac{1-\alpha}{1+\alpha}\times P \qquad \frac{2\alpha}{1+\alpha}\times P$

Given, $\alpha = 0.2$, $P = 1$

$$\text{Partial pressure of } N_2O_4 = \frac{1-0.2}{1+0.2}\times 1 = \frac{0.8}{1.2} = \frac{2}{3}$$

$$p_{NO_2} = \frac{2\times0.2}{1+0.2}\times 1 = \frac{0.4}{1.2} = \frac{1}{3}$$

$$K_p = \frac{[p_{NO_2}]^2}{[p_{N_2O_4}]} = \frac{1\times1\times3}{3\times3\times2} = \frac{1}{6}$$

10. (2)

	CO_2	$\rightleftharpoons CO$	+ $\frac{1}{2}O_2$
Initial	1	0	0
Final	$1-\alpha$	α	$\alpha/2$
Final	$4(1-\alpha)$	4α	$\alpha/2 \times 4$

$\alpha = 0.25\% = 0.25$.

Number of moles of CO $= 4\alpha = 4 \times 0.25 = 1$

11. (3) $\alpha = 50\% = \frac{50}{100} = 0.5$

	N_2	+ $3H_2$	$\rightleftharpoons 2NH_3$
Initial	1	3	0
Final	$1-\alpha$	$3-3\alpha$	2α

Total moles $= 1 - \alpha + 3 - 3\alpha + 2\alpha$

$= 4 - 2\alpha$

$= 4 - 2 \times 0.5 = 3$

12. (2) The equilibrium constant depends only upon temperature.

13. (2)

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial	1		1		0
Final	$\frac{1-\alpha}{v}$		$\frac{1-\alpha}{v}$		$\frac{2\alpha}{v}$

Since $\Delta n = 0$ $[2-(1+1)]$

$\therefore$ K does not depend on volume.

So on reducing volume to half K does not change.

$\therefore K = 50.$

14. (4) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

If the concentration of PCl_3 is doubled, it only predicts, that reaction will proceed backward. (Le-Chatlier's principle). So the concentration of Cl_2 is unpredictable.

15. (2)

	XY_2	$\rightleftharpoons$	XY	+	Y
Initial	P		0		0
Final	$P-x$		x		x

Initial $P = 600$ mm Hg, Final $P = 800$ mm Hg

Total moles $\propto$ final P.

$\therefore P - x + x + x \propto 800$

$600 - x + x + x \propto 800$

$x = 200$ mm Hg

$$K = \frac{x \times x}{P - x} = \frac{200 \times 200}{400} = 100 \text{ Hg}$$

16. (3) $K = \frac{R_f}{R_b} = \frac{0.25}{5000} = 5.0 \times 10^{-5}$

17. (3)

	2HX	$\rightleftharpoons$	$H_2(g)$	+	$X_2(g)$
At equilibrium	?		1.2×10^{-3} M		1.2×10^{-4} M

$$K = \frac{[H_2][X_2]}{[HX]^2}$$

$$10^{-5} = \frac{1.2 \times 10^{-3} \times 1.2 \times 10^{-4}}{[HX]^2}$$

$$[HX] = \sqrt{\frac{1.2 \times 1.2 \times 10^{-7}}{10^{-5}}}$$

$= 1.2 \times 10^{-1}$

$= 12 \times 10^{-2}$ M

18. (2) i. $S^{2-} + S \longrightarrow S_2^{2-}$ ...k_1

ii. $S_2^{2-} + S \longrightarrow S_3^{2-}$ ...k_2

The equation constant for the reaction,

iii. $S_3^{2-} \longrightarrow S^{2-} + 2S$,

Since eq. (iii) is obtained by reversing and adding equations (i) and (ii).

19. (4) (1) $HgCl^{\oplus} + Cl^{\ominus} \longrightarrow HgCl_2$ ... K_1

(2) $HgCl_2 + Cl^{\ominus} \longrightarrow HgCl_3^{\ominus}$ ... K_2

The eq. constant (k) for the reaction,

$2HgCl_2 \longrightarrow HgCl^{\oplus} + HgCl_3^{\ominus}$

Can be obtained by reversing equation (a) and adding to equation (b).

$$K = \frac{1}{K_1} \times K_2 = \frac{K_2}{K_1} = \frac{8.9}{3 \times 10^6} \approx 3 \times 10^{-6}$$

20. (4)

	$2NO_2$	$\rightleftharpoons$	N_2O_4
At equilibrium	0.2 kPa		0.4 kPa

$$K_p = \frac{[p_{N_2O_4}]}{[p_{NO_2}]^2} = \frac{0.4}{0.2 \times 0.2} = 10$$

21. (2) $\alpha = \frac{D - d}{d}$

D = Vapour density before dissociation

d = Vapour density after dissociation

$N_2O_4 \rightleftharpoons 2NO_2$

Vapour density of N_2O_4 before dissociation

$$(D) = \frac{14 \times 2 + 16 \times 4}{2} = \frac{92}{2} = 46$$

Vapour density after dissociation (d) = 38.3

$$\therefore \alpha = \frac{46 - 38.3}{38.3} = 0.2$$

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial	1		0
At equilibrium	$1-\alpha$		2α

Number of moles of NO_2 at eq. $= 2\alpha = 2 \times 0.2 = 0.4$

22. (2)

	N_2O_4	$\rightleftharpoons$	$2NO_2$
At equilibrium	$1-\alpha$		2α

Number of moles of $N_2O_4 = 1 - \alpha = 1 - 0.2 = 0.8$

Weight of N_2O_4 in mixture

= moles of N_2O_4 × Mw of $N_2O_4 = 0.8 \times 92 = 73.6$ g

Weight of NO_2 in mixture

= moles of NO_2 × Mw of NO_2

$= 0.4 \times 46 = 18.4$ g

Total weight $= 73.6 + 18.4 = 92.0$ g

In 92 g of mixture, number of moles of $N_2O_4 = 0.8$

In 100 g of mixture; number of moles of N_2O_4

$$= \frac{0.8 \times 100}{92} = 0.86$$

23. (2)

	$2SO_3$	$\rightleftharpoons$	$2SO_2$	+	O_2
Initial	1		0		0
At equilibrium	$1-2x$		$2x$		x

$\therefore 2x = 0.6$, $\therefore x = 0.3$

$[SO_3] = 1 - 2x = 1 - 0.6 = 0.4$

$[SO_2] = 2x = 0.6$

$[O_2] = x = 0.3$

$$K = \frac{x \times (2x)^2}{(1-2x)^2} = \frac{0.3 \times 0.6 \times 0.6}{0.4 \times 0.4} = 0.675$$

24. (3)

	W	+	X	$\rightleftharpoons$	Y	+	Z
Initial	1		1		0		0
At eq.	$1-x$		$1-x$		x		x

$K = 9$

$$K = 9 = \frac{x^2}{(1-x)^2}$$

$\therefore x = 0.75$

Moles of $y = x = 0.75$

25. (3) $A + 2B \rightleftharpoons C + \text{Heat}$

The equation shows, that it is exothermic reaction. Since the heat is released in the reaction, so the reaction is favoured in forward direction at low temperature.

$\Delta n = 1 - (2 + 1) = -2$

Since the number of moles decreases, therefore, the forward reaction is favoured at high pressure.

26. (4) Active mass = Concentration = mol L^{-1}

$$[\text{HI}] = \frac{64}{128 \times 2} = 0.25\text{ M}$$

27. (3) $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{Heat}$

$\Delta n = 2 - (1 + 3) = -2$

$\therefore K_p = K_c(RT)^{-2}$

28. (4)

29. (3) With increase in temperature, K value decreases, which means that at high temperature the reaction proceeds in backward direction or proceeds forward at room temperature. In another words, at room temperature, HI dissociates or HI is less stable than H_2 and I_2.

30. (1) $N_2 + O_2 \rightleftharpoons 2NO$ ...(i)

$NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2$ ...(ii)

Equation (ii) is obtained by reversing equation (i) and dividing by 2.

$$\therefore K_2 = \frac{1}{(K_1)^{1/2}}$$

$$\Rightarrow (K_2)^2 = \frac{1}{K_1}$$

$$\Rightarrow K_1 = \frac{1}{(K_2)^2} = \left(\frac{1}{K_2}\right)^2$$

31. (1) $\Delta G^\ominus = -2.303\, RT \log K$

$= -2.303 \times 2 \times 298 \log 10^{-8}$

$= -2.303 \times 2 \times 298 \times -8$ cal

$= 10980$ cal $= 10.98$ kcal

32. (4) Effect of catalyst is only to alter the speed of the reaction, it does not effect the equilibrium constant and concentration of reactant or product.

33. (3) Rate of forward reaction = Rate of backward reaction i.e., when $R_f = R_b$, equilibrium is established.

34. (4) At equilibrium, amount of NH_3 formed is equal to the amount of NH_3 decomposed into H_2 and N_2.

35. (3) K does not depend on initial concentration of R or P.

36. (1) As the temperature is increased, solubility of solid in liquid increases and hence equilibrium shifts to the right and hence the amount of solid decreases.

Solid + aq $\longrightarrow$ Solution

37. (2) $N_2 + O_2 \rightleftharpoons 2NO + \text{Heat}$

The above equation shows that the reaction is endothermic. Endothermic reactions are forward in forward direction at high temperature.

38. (2) $A + B \rightleftharpoons C + D$

According to Le Chatelier's principle, as the concentration of the products are increased, the reaction proceeds in the backward direction.

39. (1)

$$\begin{array}{lcccc} & A(g) & + & 2B(g) & \rightleftharpoons C(g) \\ \text{At eq.} & 0.06\text{ M} & & 0.12\text{ M} & 0.216\text{ M} \end{array}$$

$$K = \frac{[C]}{[B^2][A]} = \frac{0.216}{0.12 \times 0.12 \times 0.06} = 250$$

40. (2)

$$\begin{array}{lccccccc} & A & + & B & \rightleftharpoons & C & + & D \\ \text{Initial} & 4 & & 4 & & 0 & & 0 \\ \text{Final} & 4-x & & 4-x & & x & & x \end{array}$$

$x = 2$

$\therefore [A] = 4 - 2 = 2, \quad [B] = 4 - 2 = 2$

$[C] = 2, \quad [D] = 2$

$$K = \frac{[C][D]}{[A][B]} = \frac{2 \times 2}{2 \times 2} = 1$$

41. (4) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_c = P_{CO2}$, therefore, K_c only depends upon concentration of CO_2 as long as temperature remains constant and both $CaCO_3(s)$ and $CaO(s)$ are present.

42. (2) Catalyst does not change the extent of reaction, and hence does not alter the value of K.

43. (1) In which $\Delta n = 0$

i. $\Delta n = 2 - (1 + 1) = 0$ **ii.** $\Delta n = 2 - (2 + 1) = -1$

iii. $\Delta n = 2 - (1 + 3) = -2$ **iv.** $\Delta n = 1 - (1 + 1) = -1$

44. (4) $\alpha = 50\% = \frac{50}{100} = 0.5$

$$\begin{array}{lccccc} & 2HI & \rightleftharpoons & H_2 & + & I_2 \\ \text{Initial} & 2 & & 0 & & 0 \\ \text{Final} & (2-2\alpha) & & \alpha & & \alpha \end{array}$$

$$K = \frac{\alpha^2}{(2-2\alpha)^2} = \frac{0.5 \times 0.5}{(2 - 2 \times 0.5)^2} = 0.25$$

45. (1) $A(g) \rightleftharpoons B(g) + C(g)$

(1) With increase of temperature K_p increases, i.e., with increase of temperature, the reaction is favoured in forward direction and hence reaction is endothermic. Thus statement (1) is incorrect.

(2) Increase of temperature favours forward reaction and hence the formation of B increases. Correct statement.

(3) $\Delta n = 1 + 1 - 1 = 1$

Δn = +ve, i.e., with the increase of pressure, reaction is favoured backward direction and hence the formation of $A(g)$ increases. Correct statement.

(4) As from the above statement in (i) and (iii), the reaction is favoured backward with decrease of temperature and increase of pressure. Correct statement.

46. (3)

$$\begin{array}{lccccc} & 2AB_3(g) & \rightleftharpoons & A_2(g) & + & 3B_2(g) \\ \text{Initial} & 8 & & 0 & & 0 \\ \text{At eq.} & \frac{8-2x}{1} & & \frac{x}{1} & & \frac{3x}{1} \end{array}$$

Since volume = 1 dm^3 = 1 L

At eq. $[A_2] = 2$ mol $= x$

$\therefore [AB_3] = 8 - 2 \times 2 = 4$ M

$[A_2] = 2$ M

$[B_2] = 3 \times 2 = 6$ M

$$K = \frac{[B_2]^3[A_2]}{[AB_3]^2} = \frac{6 \times 6 \times 6 \times 2}{4 \times 4} = 27 \text{ mol}^{-2}\text{ L}^{-2}$$

47. (4)

	$XY(g)$	$\rightleftharpoons$	$X(g)$	+	$Y(g)$
Initial	1		0		0.2
At eq.	$1 - x$		x		$0.2 + x$

At eq. $[X] = 0.2 + x = 0.6$

$$\therefore x = 0.4 \text{ mol} = \frac{0.4}{1} = 0.4 \text{ M}$$

$$[XY] = 1 - 0.4 \text{ mol} = 0.6 \text{ mol} = \frac{0.6}{1} = 0.6 \text{ M}$$

$$[X] = x = 0.4 = \frac{0.4}{1} = 0.4 \text{ M}$$

$$K = \frac{[X][Y]}{[XY]} = \frac{0.4 \times 0.6}{0.6} = 0.4 \text{ mol L}^{-1}$$

48. (2, 4)

Since $\Delta H < 0$ i.e., $\Delta H < -$ve,

Reaction is exothermic, so lowering of temperature will shift equilibrium towards right. Statement (d) is correct and also the concentration of reactants decreases and products increases. So statement (b) is also correct.

49. (1) $\Delta n = 2 - 1 = 1$

(1) That is, with the decrease of pressure, reaction shifts towards right, i.e. proportions of NO_2 increases. Statement (1) is correct.

(2) Value of K increases with increase of temperature and hence reaction is endothermic, i.e., $\Delta H = +$ve

Hence statement (2) is incorrect.

(3) $K_p = \dfrac{[p_{NO_2}]^2}{[p_{N_2O_4}]} = \dfrac{\text{atm}^2}{\text{atm}} = \text{atm}$

Hence statement (c) is incorrect.

(4)

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial	1 atm		0
At eq.	$1 - \alpha$		2α

$$K_p = \frac{(2\alpha)^2}{1 - \alpha} = 1.7 \times 10^3 \text{ at 500 K}$$

$[(1 - \alpha \approx 1)$, since α is small$]$

$4\alpha^2 = 1.7 \times 10^3$

$$\alpha_1 = \sqrt{\frac{1.7 \times 10^3}{4}}$$

$\alpha = 0.206 \times 10^2$

When the pressure was 1 atm, now let it be 2 atm (100% increase).

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial	2		0
At eq.	$2 - \alpha$		2α

$$K_p = \frac{(2\alpha)^2}{2 - \alpha} = 1.7 \times 10^3 \text{ at 500 K}$$

$[2 - \alpha \approx 2$, since α is small$]$

$$\frac{4\alpha^2}{2} = 1.7 \times 10^3$$

$$\alpha_2 = \sqrt{\frac{1.7 \times 10^3}{2}}$$

$$\frac{\alpha_2}{\alpha_1} = \sqrt{\frac{1.7 \times 10^3 \times 4}{2 \times 1.7 \times 10^3}} = \sqrt{2} = 1.4$$

$\therefore$ When the pressure is increased 100% the decrease in α is 1.4 times which is not 50%. Hence statement is wrong.

50. (3) Volume = 3 L

	X	+	Y	$\rightleftharpoons$	$3Z$
At eq.	$\frac{1}{3}$		$\frac{2}{3}$		$\frac{4}{3}$

$$K = \frac{[Z]^3}{[X][Y]} = \frac{\left(\frac{4}{3}\right)^3}{\left[\frac{2}{3}\right]\left[\frac{1}{3}\right]} = 10.67$$

(1) $Q = 10$, $\therefore Q < K$

The reaction proceed forward direction to attain the equilibrium value of K

(2) $Q = 15$, $\therefore Q < K$

The reaction proceeds backward direction to attain the equilibrium value of K (10.67).

(3) $Q = 10.67$, $\therefore Q = K$

The system is at equilibrium

51. (1)

	$FeO(s)$	+	$CO(g)$	$\rightleftharpoons$	$Fe(s)$	+	$CO_2(g)$
At eq.	—		0.025		—		x
	solid				solid		

$$K_c = \left[\frac{CO_2(g)}{CO(g)}\right] = \frac{x}{0.025} = 5.0 \text{ (Given)}$$

$\therefore x = 0.125$ M

$[CO_2] = 0.125$ M

52. (2, 4)

(1) $\Delta n = 1 + 1 - 1 = 1$

(2) $\Delta n = 2 - (1 + 1) = 0$

(3) $\Delta n = 1 - 0 = 1$

(4) $\Delta n = 1 + 1 - (1 + 1) = 0$

Δn is zero in (2) and (4), so (2) and (4) are not effected by pressure.

53. (4) Since the given equilibrium involves $\Delta n_g = 0$, there will be no effect of adding an inert gas and decreasing the volume of the container. A catalyst can help in achieving the equilibrium rapidly without affecting the equilibrium amounts of the species involved in the reaction.

Only increasing the amount of a reactant can shift the equilibrium amount of a product.

54. (1) The given reaction will be exothermic in nature due to the formation of three X-Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species. Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentration of the species in the chemical reaction.

55. (4) For the reaction $A + B \longrightarrow C + D$, the reaction quotient is defined as

$$Q = \frac{[C][D]}{[A][B]}$$

In the initial stages of the reaction, the concentrations of C and D increase while those of A and B decrease. Hence, the value of Q increases with time.

56. (4)

Multiple Correct Answers Type

1. (2, 3)

2. (1, 3)

Increasing the concentration of reactants favours the product formation.

3. (1, 2, 4)

$$Q = \frac{[S_2]^4}{[S_8]} = \frac{(0.2)^4}{(2)} = 8 \times 10^{-4};\ K_c = 6.3 \times 10^{-6}$$

$$\therefore K_p = K_c \times (RT)^{\Delta n} = 6.3 \times 10^{-6} \times (0.0821 \times 900)^3 = 2.55$$

Thus, reaction proceed in backward direction since $Q > K_c$

4. (1, 2, 3, 4)

$$\Delta G = \Delta G^{\ominus} + 2.303\ RT \log Q$$

$$\Delta G = 2 \times G^{\ominus}_{NO_2} - G^{\ominus}_{N_2O_4} = 2 \times 50 - 100 = 0$$

$$\therefore \Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \log \frac{22}{5}$$

$$= 0 - 0.55\ \text{kJ}$$

$\therefore \Delta G = -0.55$ kJ, i.e., reaction proceed in forward direction

Also $\Delta G^{\ominus} = 0 = 2.303\ RT \log K\ \therefore\quad K = 1$

$$\begin{array}{lccc} \text{Now,} & N_2O_4 & = & 2NO_2 \\ & 5 & & 2 \\ & 5 - x & & 2 + 2x \end{array}$$

$$\therefore K_p = \frac{(P_{NO_2})}{(P_{N_2O_4})} = 1 = \frac{(2 + 2x)^2}{5 - x} \text{ or } x = 0.106$$

5. (1, 2, 3, 4)

$$\begin{array}{lcccccc} & A_2 & \rightleftharpoons & 2C & + & D \\ \text{Initial} & 1 & & 0 & & 0 \\ \text{At equilibrium} & 1 - \alpha & & 2\alpha & & \alpha \end{array}$$

$$K_p = (2\alpha)^2 \alpha \times \left[\frac{P}{\Delta n}\right]^2 = \frac{4\alpha^3 P^2}{(1 + 2\alpha)^2}$$

Use $2.303 \log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$ for effect temperature on K

6. (2, 4) The van't Hoff equation is $K = Ae^{-\Delta H/RT}$

$$\text{or} \quad \frac{d \ln K}{\partial T} = \frac{\Delta H}{RT^2}$$

7. (1, 2, 3, 4)

$$\begin{array}{ccccc} A(s) & \rightleftharpoons & 2B(g) & + & C(g) \\ & & 2\alpha + 2\alpha' & & \alpha \\ A'(s) & \rightleftharpoons & 2B & + & D \\ & & 2\alpha' + 2\alpha & & \alpha' \end{array}$$

$$K_{p_1} = (2\alpha + 2\alpha')^2 \times \alpha \times \left[\frac{P}{(3\alpha + 2\alpha')}\right]^3$$

$$K_{p_2} = (2\alpha + 2\alpha')^2 \times \alpha' \times \left[\frac{P}{(3\alpha' + 2\alpha)}\right]^3$$

$$\frac{K_{p_1}}{K_{P_2}} = \frac{[3\alpha' + 2\alpha]^3}{[3\alpha + 2\alpha]^3} \times \frac{\alpha}{\alpha_1}$$

Also, $K_{p_1} = (P'_B)^2 \times P'_c$

$K_{p_2} = (P'_B)^2 \times P'_p$

$$\text{or} \quad \frac{P'_c}{P'_D} = \frac{K_{p_1}}{K_{p_2}} = \frac{8 \times 10^{-2}}{2 \times 10^{-2}} = 4$$

Also, $P'_B = 2 \times (P'_c + P'_D)$

$K_{p_1} > K_{p_2}\ \therefore \alpha > \alpha_1$

8. (2, 3, 4) **9. (2, 3, 4)**

10. (1, 2, 4) $K_p = K_c(RT)^{\Delta n}$, when $\Delta n \neq 0$, $K_p \neq K_c$

11. (2, 3, 4) **12. (2, 3, 4)** **13. (1)**

14. (1, 3, 4), K_p depends upon temperature only.

15. (2, 3, 4) **16. (1, 3, 4)** **17. (1, 2)**

18. (2, 3)

19. (1, 2)

$$\Delta G^{\ominus} = -nRT \ln \text{K and } 2.303 \log \text{K} = \frac{-\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R}$$

20. (1, 2, 3), $K_p = K_c(RT)^{\Delta n}$

21. (1, 2, 3)

22. (2, 3, 4)

$$K_1 = \frac{K_f}{K_b} = \frac{2 \times 10^{-2}}{4 \times 10^{-3}} = 5 \text{ at } 300\text{ K}$$

$$K_2 = \frac{K_f}{K_b} = \frac{4 \times 10^{-2}}{16 \times 10^{-4}} = 25 \text{ at } 400\text{ K}$$

$$\therefore \quad 2.303 \log \frac{25}{5} = \frac{\Delta H}{2} \times \left[\frac{400 - 300}{400 \times 300}\right]$$

or $\Delta H = 3.86$ kcal

(2, 3, 4) **24. (1, 2, 4)** **25. (1, 2, 4)**

(3, 4)

ed Comprehension Type

1. (1) Shift in product side.

2. (2)

3. (1) Shift in product side because on increasing the pressure of the system, the equilibrium shift to lesser number of molecules side, i.e., the product side.

4. (2) Addition of Ni^{2+} causing more blue colour means reaction moving in the forward direction.
$\Rightarrow [Ni(NH_3)_6]^{2+}$ has increased and NH_3(unreacted) was present initially.

5. (4) Addition of NH_3 causing more blue colour means reaction moving in the forward direction.
$\Rightarrow [Ni(NH_3)_6]^{2+}$ has increased and Ni^{2+} (unreacted) was present initially.

6. (2) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g);$

$$\quad 27\times10^{-2} \qquad X$$

$K_c = 27 \times 10^{-2} X = 8.91 \times 10^{-2}$

$$X = \frac{8.91\times10^{-2}}{2.7\times10^{-1}} = 3.3\times10^{-1}$$

Number of mol of $NH_3 = 0.27$

$H_2S = 0.33$

$N_2 = 0.03$

$H_2 = 0.09$

$$X_{H_2} = \frac{0.09}{0.72} = \frac{1}{8}$$

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

$$3a \qquad \frac{1}{3}a \qquad a$$

$$K_c = \frac{(a/3)a^3}{(3a)^2} = \frac{a^4}{3}\times\frac{1}{9a^2}$$

$$\frac{a^2}{27} = 3\times10^{-4}$$

$\therefore a^2 = 81 \times 10^{-4}$

$a = 9 \times 10^{-2}$

7. (3) Amount of $NH_4HS(s)$ dissociated amount of $H_2S(g)$ present at equilibrium
$\therefore$ Amount of $NH_4HS(s)$ dissociated = 0.33 mol
%(by weight) of $NH_4HS(s)$ dissociated

$$= \frac{0.33}{1}\times100 = 33\%$$

8. (1) Amount of the gases present at equilibrium = weight of $NH_4HS(s)$ dissociated
$\therefore$ Amount of the gases present $= 0.33 \times 51$ g
Volume of the gases = 1L
$\therefore$ Density of the gaseous mixtures

$$= \frac{0.33\times51}{1}\,gL^{-1} = 16.83\text{ g L}^{-1}$$

9. (1) **10. (3)** **11. (3)**

12. (2) $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

13. (2) It is an exothermic reaction. Hence, the value of K_c decreases with increase in temperature.

14. (1) $K_p = K_c(RT)^{\Delta n} = K_c(RT)^{-2}$
$\therefore K_c = K_p(RT)^2$

15. (1) Presence of catalyst does not affect the concentration of various species at equilibrium.

16. (3) $[N_2] = \dfrac{2}{5}M;\ [H_2] = \dfrac{2}{5}M;\ [NH_3] = \dfrac{2}{5}M$

$$Q_c = \frac{[NH_3]}{[N_2][H_2]^3} = \frac{(2/5)^2}{(2/5)(2/5)^3} = (2/5)^{-2} = 6.25$$

Since Q_c is greater than K_c (1.2) the reaction takes place in backward direction.

17. (1) **18. (2)**

19. (1) $K_p = K_c(RT)^{\Delta n};\ \Delta n = 3 - 1 = 2$
$\therefore K_p = K_c(RT)^2$

$$\text{or } K_c = \frac{K_p}{(RT)^2} = \frac{38}{(8.314\times700)^2}$$

20. (2) On increasing pressure, the equilibrium shift in such side which have lesser number of molecules i.e., backward direction.

21. (3) Reaction shift in forward direction.

22. (2) $P_{NH_3} = P_{HCl} = \dfrac{0.820}{2}$ bar

$\therefore K_p = P_{NH_3} \times P_{HCl} = 0.41 \times 0.41 = 0.168$

23. (1) Moles of gases, $n = \dfrac{PV}{RT} = \dfrac{0.820\times4}{0.083\times300} = 0.132$ mol

Moles of NH_3 = Moles of HCl $= \dfrac{0.132}{2} = 0.066$

Moles of NH_4Cl decomposed = Moles of $NH_3 = 0.066$

Moles of NH_4Cl initially present $= \dfrac{6.250}{51} = 0.122$

Moles of NH_4Cl left $= 0.122 - 0.066 = 0.056$

Mass of NH_4Cl left behind $= 0.056 \times 51 = 2.856$ g

24. (1) According to Le Chatelier's principle, with increase in volume, the equilibrium shifts in forward direction.

25. (1) Since, the decomposition is an endothermic process hence on increasing temperature the equilibrium shift in forward direction.

26. (2) For endothermic reaction, K_p decreases with decrease in temperature.

27. (1, 2) $K_p = K_c(RT)^{\Delta n}$

28. (1, 2) K_p for reaction (1) $= \dfrac{P_{(PCl_3)}\times P_{Cl_2}}{P_{PCl_5}}$ = atm

K_p for reaction (2) $= \dfrac{P_{(AB)}\times P_{(B)}}{P_{(AB_2)}}$ = atm

$\therefore$ 1, 2

29. (2) For reaction (2)

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^{-2}$$

$$\therefore K_c = K_p(RT)^2$$

$$\therefore K_p < K_c$$

30. (4) $K_p = K_c(RT)^{\Delta n}$

$$= K_c\,(RT)^{-2} = \frac{K_c}{(RT)^2}$$

or $\dfrac{K_p}{K_c} = \dfrac{1}{(RT)^2}$

31. (4)

32. (3) $K_3 = K_1 \times K_2$

33. (4) From reaction (i) and (ii), we get

$$2H_2(g) + 2CO_2(g) \rightleftharpoons 2CO(g) + 2H_2O(g);$$

$K = 1.7 \times 10^{-12}$

And hence $H_2 + CO_2 \rightleftharpoons CO + H_2O$;

$$K = \frac{1.7 \times 10^{-12}}{2} = 0.85 \times 10^{-12}$$

34. (2) $K_3 = K_1 \times K_2$

35. (1) $H_3PO_4 \xrightarrow{K_1} H^{\oplus} + H_2PO_4^{\ominus}$

$$H_2PO_4^{\ominus} \xrightarrow{K_2} H^{\oplus} + HPO_4^{2-}$$

$$HPO_4^{2-} \xrightarrow{K_3} H^{\oplus} + PO_4^{3-}$$

$\therefore$ For $H_3PO_4 \xrightarrow{K} 3H^{\oplus} + PO_4^{3-}$

$K = K_1 \times K_2 \times K_3$

36. (4) $K = \dfrac{K_2}{K_1}$

37. (4) $K_p = K_c(RT)^{\Delta n} = K_c(RT)^{(2-4)}$

$$= K_c(RT)^{-2} = \frac{K_c}{[(0.082) \times (300)]^2}$$

38. (2) $T_1 > T_2 > T_3$

The % yield will decrease with rise in temperature since it is exothermic.

39. (3)

40. (3) $K_p = \dfrac{1}{1.44 \times 10^{-5}}$

41. (2)

42. (3) When $Q > K$, the reaction proceeds in backward direction.

43. (1) $2A + B \rightleftharpoons 3C$

$$[A] = \frac{\text{Moles}}{\text{Volume}} = \frac{2}{4}$$

$$[B] = \frac{1}{4}$$

$$[C] = \frac{4}{4} = 1$$

$$\therefore Q = \frac{[C]^3}{[A]^2\,[B]} = \frac{(1)^2}{\left(\frac{1}{2}\right)^2\left(\frac{1}{4}\right)} = 16$$

Therefore $Q < K_c$, hence reaction will favour forward direction.

44. (2) $Q_p > K_p$ $\therefore$ backward direction.

45. (3) $Q_p < K_p$

46. (1) In backward direction $Q > K$

In forward direction $Q < K$

At equilibrium $Q = K$

47. (2) $CuSO_4.5H_2O \rightleftharpoons CuSO_4.3H_2O + 2H_2O(g)$

$p_{H_2O} = 7.8$ mm

$$\Rightarrow K_p = (p_{H_2O})^2 = (7.8)^2 = 60.84$$

48. (1) $CuSO_4.5H_2O \rightleftharpoons CuSO_4.3H_2O + 2H_2O(g)$

$K_p = 60.84$

$CuSO_4.3H_2O \rightleftharpoons CuSO_4.H_2O + 2H_2O(g)$

$$K'_p = (p_{H_2O})^2 = (5.6)^2 = 31.56\,,\ p_{H_2O} = 5.6\text{ mm}$$

The ratio $\dfrac{K_p}{K'_p} = \dfrac{60.84}{31.36} = 1.9$

49. (2) Dehydration of $CuSO_4.5H_2O$ is favourable at low humidity in air, high temperature and it decreases with increasing partial pressure of water vapours i.e. p_{H_2O}.

50. (3) The concentration of [*Y*]

is constant $\Rightarrow y$ must be solid. The concentration of *X* decreases white the concentration of *Z* increases

Therefore *X* must be reactant and *Z* must be product.

$\therefore$ (3)

51. (3) $X(g) + Y(s) \rightleftharpoons Z(g)$

From graph

$t = t_{Eq}$ 6 4

(concentrated)

$$\therefore K_c = \frac{[Z]}{[X]} = \frac{4}{6} = \frac{2}{3}$$

$\therefore$ (3)

52. (4) $X(g) + Y(s) \rightleftharpoons Z(g)$

Moles left

at $t = t_{Eq}$ $6 \times 2 = 12$ – $4 \times 2 = 8$

To get 8 moles of *Z*, moles of *Y* reacted = 8

53. (1) $X(s) \rightleftharpoons A(g) + C(g)$;

20 mm 20 mm

$K_{p_1} = 20 \times 20 = 400$ mm^2

and

$Y(s) \rightleftharpoons B(g) + C(g)$;

30 mm 30 mm

$K_{p_2} = 30 \times 30 = 900$ mm^2

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{4}{9}$$

Hence, (1) is the correct answer.

54. (3) In mixture, solid X and Y dissociate simultaneous,

$$\begin{array}{llcl} X(s) \rightleftharpoons & A(g) & + & C(g) \\ & p_1 & & (p_1+p_2) \\ Y(s) \rightleftharpoons & B(s) & + & C(s) \\ & p_2 & & (p_2+p_1) \end{array}$$

$$\therefore \frac{K_{p_1}}{K_{p_2}} = \frac{p_1}{p_2} = \frac{4}{9}$$

Hence, (3) is the correct answer.

5. (2) $K_{p_1} = p_1(p_1 + p_2)$

$K_{p_2} = p_2(p_1 + p_2)$

On solving $p_1 = 23.09$, $p_2 = 51.75$

$\therefore p_1 + p_2 = 74.84$ mm

Hence, (2) is the correct answer.

atrix Match Type

1. **(a → s)** At equilibrium $Q = K$.

(b → q, r) When $Q < K$, reaction proceeds in forward direction.

(c → q, t) When $Q > K$, reaction proceeds in backward direction.

(d → p) When $K >> 1$, reaction is about to complete.

2. **(a → q; b → p; c → r, s)**

(c → r, s)

$K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2 - 4 = -2$

$\therefore K_p = K_c(RT)^{-2}$ or $K_c > K_p$

3. **(a → p, r; b → p, r; c → q; d → s)**

For $A + B \rightleftharpoons [AB]$

Hint: $K_c = \dfrac{[A][B]}{[AB]} = \dfrac{[\text{mol L}^{-1}]\,\cancel{[\text{mol L}^{-1}]}}{\cancel{[\text{mol L}^{-1}]}} = [\text{mol L}^{-1}]$

Use above expression for all equation.

4. **(a → p, s; b → p, r, s; c → q, r; d → p, s)**

5. **(a → p, r)** it is endothermic reaction hence on increasing temperature reaction proceed in forward direction. On addition of inert gas, at constant pressure also favour product side according to Le Chatelier principle.

(b → q, r, s) it is exothermic reaction hence on increasing temperature reaction proceed in backward direction.

(c → p) endothermic reaction therefore on increasing temperature reaction proceed in product side.

(d → s) exothermic reaction therefore on increasing temperature reaction proceed in backward side.

6. **(a → r)** $A \xrightarrow{K_1} B$ for reverse reaction $B \xrightarrow{K} A$;

$K = \dfrac{1}{K_1}$

(b → p) $K = (K)^{1/2}$

(c → p) $K = K^2$

7. **(a → p, s; b → p, s; c → q, r; d → p, r)**

According to Le Chatelier principle endothermic reaction proceed in forward direction on increasing temperature while the exothermic reaction proceed in backward direction on increasing temperature.

8. **(a → s)** $K_p = K_c(RT)^{\Delta n}$; $\Delta n = (2 - 2) = 0$

$\therefore K_p = K_c$

(b → r) $K_p = K_c(RT)^{\Delta n}$; $\Delta n = (2 - 4) = -2$

$\therefore K_p = K_c(RT)^{-2}$

(c → p) $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2 - 1 = 1$

$\therefore K_p = K_c(RT)$

(d → q) $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2 - 0 = 2$

$\therefore K_p = K_c(RT)^2$

9. **(a → p)** $\Delta n = n_P - n_R > 0$; the number of molecules in product side are higher than reactant side hence according to Le Chatelier principle on increasing the pressure equilibrium shift to lesser number of molecules side.

(b → r) When there is no change in volume ($\Delta V = 0$) then addition of inert gas does not change the equilibrium.

(c → s) $K_p = K_c(RT)^{\Delta n}$, when $\Delta n = 0$

$\therefore K_p = K_c(RT)^{\circ}$ or $K_p = K_c$

(d → q)

10. **(a → p, r; b → p, r; c → q; d → s)**

According to Le Chatelier principle, on increasing the pressure the reaction shift in the direction which have lesser number of molecules.

11. **(a → t; b → u; c → p; d → v; e → q; f → s; g → r)**

Numerical Value Type

1. **(4)** 0 At equilibrium $\Delta G = 0$

2. **(1)** $K_p = K_c(RT)^{\Delta n}$

when $\Delta n = 0$

$K_p = K_c$

3. **(2)** We know that $K = \dfrac{K_f}{K_b}$

$$\therefore K = \frac{4 \times 10^2}{2 \times 10^2} = 2$$

4. **(2)** For $A + B \rightleftharpoons AB$; $K = 0.5$

For $AB \rightleftharpoons A + B$; $K' = ?$

$$\therefore K' = \frac{1}{K} = \frac{1}{0.5} = 2$$

5. **(1)** $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Initial	1	1	0	0
At equ.	$1-\frac{1}{2}$	$1-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

$$K = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} = \frac{\frac{1}{2} \times \frac{1}{2}}{\frac{1}{2} \times \frac{1}{2}} = 1$$

6. (1) For $A + B \rightleftharpoons AB$

$$K = \frac{[AB]}{[A][B]}$$

When $2A + 2B \rightleftharpoons 2AB$

$K = 2AB$

7. (1) At equilibrium $\Delta G = 0$

$\Delta G = -nRT \ln K$

$0 = -nRT \ln K$

or $K = 1$

Archives

JEE Main

Single Correct Answer Type

1. (1)

$$\begin{array}{lcc} & CO_2(g) + C(s) \rightleftharpoons & 2CO(g) \\ \text{Initial} & 0.5 \text{ atm} & - \\ \text{At equilibrium} & (0.5 - p) & 2p \text{ atm} \end{array}$$

This is a case of heterogeneous equilibrium.

$C(s)$ being solid is not considered.

Total pressure of CO_2 and CO gases.

$$p_{CO_2} + p_{CO} = P_{total}$$

$$0.5 - (p + 2p) = 0.8, p = 0.3 \text{ atm}$$

$$\therefore \quad p_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$

$$p_{CO} = 2p = 0.6 \text{ atm}$$

$$K_P = \frac{p^2_{CO}}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8 \text{ atm}$$

2. (4)

For the reaction

$N_2 + O_2 \rightarrow 2NO \quad K_c = 4 \times 10^{-4}$

Hence for the reaction

$$NO \rightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2$$

$$K'_c = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{100}{2} = 50$$

3. (2)

By using this formula, equilibrium constant,

$K_P = K_c (RT)^{\Delta ng}$

Where Δn_g = (no. of moles of products) – (no. of moles of reactants)

For the given reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$\Delta n_g = 1 - \left[\frac{1}{2} + 1\right] = 1 - \left[\frac{3}{2}\right] = -\frac{1}{2}$$

4. (2)

$\Delta G = \Delta G^\circ + RT \ln Q$

$= 2494.2 + 8.314 \times 300 \ln 4$

$= \text{Positive } \Delta G = RT \ln \dfrac{Q}{K}$

Since, ΔG is positive so, $Q > K$, so reaction shifts in reverse direction.

5. (4)

$$A + B \rightleftharpoons C + D \qquad K = 100$$

$$Q = \frac{1 \times 1}{1 \times 1} = 1$$

$\because \ Q < K$ so reaction moves in forward reaction

$$\begin{array}{lcccc} & A + & B \rightleftharpoons & C + & D \\ \text{Initial} & 1 & 1 & 10 & 10 \\ \text{At equ.} & 1-x & 1-x & 1+x & 1+x \end{array}$$

$$\frac{(1+x)^2}{(1-x)^2} = 100 \Rightarrow \frac{1+x}{1-x} = 10$$

$$1 + x = 10 - 10x \Rightarrow x = \frac{9}{11}$$

$$\therefore [D] = 1 + x = 1 + \frac{9}{11} = 1.818 \text{ M}$$

6. (1) $[H_2S] = 0.10$ M

$[HCl] = 0.20 \text{ M} \Rightarrow [H^+] = 0.2$ M

$H_2S \rightleftharpoons H^+ + HS^- \quad K_1 = 1.0 \times 10^{-7}$

$H_2S \rightleftharpoons H^+ + S^{2-} \quad K_2 = 1.2 \times 10^{-13}$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K = K_1K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Note : If equations are added equilibrium constants are multiplied.

$$[S^{2-}] = \frac{1 \times 10^{-7} \times 1.2 \times 10^{-13} \times 0.1}{[0.2]^2} = 3 \times 10^{-20}$$

7. (1) $K = Ae^{-\Delta H/RT}$

$$\ln K = \ln A - \frac{\Delta H}{RT}$$

$$\ln K = -\frac{\Delta H}{R} \times \frac{1}{T} + \ln A$$

For exothermic reaction K increases with decrease in temperature.

This means K increases with increase in $\dfrac{1}{T}$. That is shown by graph A and B.

JEE Advanced

Single Correct Answer Type

1. (4) For reaction $\quad SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$

$$\Delta n_g = \left[1 - \left(1 + \frac{1}{2}\right)\right] = -\frac{1}{2} = x$$

2. (3) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3 \ \Delta H < 0$ (exothermic).

For exothermic reaction, high temperature favours the reaction in backward direction i.e. yield of reaction decreases.

3. **(4)**

$$\Delta G_{Rx^n} = 2\Delta G_{NO_2} - 2\Delta G_{NO}$$

$$\Delta G_{NO_2} = \Delta G_{NO} + \frac{1}{2}\Delta G_{Rx}$$

$$= \Delta G_{NO} + \frac{1}{2}(-RT \ln_e K_p)$$

$$= 0.5\,[2 \times 86000 - R(298) \ln_e (1.6 \times 10^{12})]$$

Multiple Correct Answers Type

1. **(2, 3, 4)**

$$2Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$$

$Cl^{\ominus}$ and $CN^{\ominus}$ both make precipitate with Cu^{I} and hence drive the reaction to the left.

Cupric thiocyanate $Cu(SCN)_2$, black power, insoluble in water, readily turning into cuprous thiocyanate Cu(SCN) a whitish yellow powder, hence it also drives the equilibrium to the left.

2. **(1, 2, 4)**

For the equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant (K) is independent of initial amount of $CaCO_3$ where as at a given temperature is independent of pressure of CO_2. ΔH is independent of catalyst and it depends on temperature.

Hence (1), (2) and (4) are correct.

3. **(2, 3)**

With increase in temperature, the value of *K* for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases.

With increase in temperature, the of *K* for exothermic reaction decreases because favorable change in entropy of the surrounding decreases.

Linked Comprehension Type

1. **(2)**

$$X_2\,(g) \rightleftharpoons 2X\,(g)$$

Initial: 1   0

At eq: $1 - \frac{\beta_e}{2}$ β_e

Total number of moles at equilibrium.

$$\Rightarrow 1 - \frac{\beta_e}{2} + \beta_e \Rightarrow 1 + \frac{\beta_e}{2}$$

$$[p_x = P_{total} \times \chi_x = 2\text{bar} \times \left(\frac{\beta_e}{1 + \frac{\beta_e}{2}}\right)$$

$$[p_{x2} = P_{total} \times \chi_{x2} = 2\text{bar} \times \left(\frac{1 - \frac{\beta_e}{2}}{1 + \frac{\beta_e}{2}}\right)$$

$$K_p = \frac{(p_x)^2}{p_{x_2}} = (2)^2\left(\frac{\beta_e}{1 + \frac{\beta_e}{2}}\right)^2 \Bigg/ \frac{\left(1 - \frac{\beta_e}{2}\right) \times 2}{1 + \frac{\beta_e}{2}}$$

$$= \left(\frac{2\beta_e^{\,2}}{1 - \frac{\beta_e}{4}}\right)$$

$$K_p = \frac{8\beta_e^{\,2}}{4 - \beta_e^{\,2}}$$

2. **(3)**

(1) True: According to Le Chatelier's principle if $\Delta n = +ve$, decrease in total pressure (or increase in V) shifts the equilirbrium to right i.e., will result in the formation of more mole of gaseous X.

(2) True

(3) False:

If $\beta_{eq} = 0.7$

$$K_p = \frac{8 \times (0.7)^2}{4 - (0.7)^2} = \frac{3.92}{3.15} > 1$$

which can't be possible as $\Delta G^{\ominus} > 0$ ($\Rightarrow K_p < 1$).

[$\Delta G^{\ominus}$ = +ve, means reaction is not feasible, so K_p should be less than one]

∴ **Therefore option (3) is incorrect.**

Alternatively,

There is no data given to find β_{eq} exact value.

$$\Delta G^{\ominus} = -2.303\,RT \log K_p$$

$$\log K_p = 1$$

$$K_p < 1$$

∴ **Therefore, option (3) is incorrect.**

(4) True

Chapter 8

Concept Application Exercises

Exercise 8.1

1. **(1)** mmole of NaOH = $25 \times 0.1 = 2.5$

i. 20 mL of 0.1 M HCl is added.

mmol of HCl = $20 \times 0.1 = 2$

mmol of NaOH left

$= 2.5 - 2.0 = 0.5$ mmol

Volume = $25 + 20 = 45$ mL

$$[\overset{\ominus}{O}H] = \frac{0.5 \text{ m mol}}{45 \text{ mL}} \approx 0.01 = 10^{-2} \text{ M}$$

pOH = 2, pH = 12

ii. 24 mL of 0.1 M HCl is added.

mmol of HCl = $24 \times 0.1 = 2.4$

mmol of NaOH left = $2.5 - 2.4 = 0.1$

$$[\overset{\ominus}{O}H] = \frac{0.1}{(25+24)} = 0.002 = 2 \times 10^{-3}\text{M}$$

$\text{pOH} = -\log[2 \times 10^{-3}] = -0.3 + 3 = 2.7$

$\text{pH} = 14 - 2.7 = 11.3$

2. **(2)** NH_3

3. **(1)** mmol of HCl = $75 \times \frac{1}{5} = 15$

mmol of NaOH = $25 \times \frac{1}{5} = 5$

mmole of HCl left = $15 - 5 = 10$

Volume = $75 + 25 = 100$

$$[H^{\oplus}] = \frac{10}{100} = 0.1 = 10^{-1}\text{M}$$

pH = 1

(2) mmol of HCl = $10 \times \frac{1}{10} = 1$

mmol of NaOH = $90 \times \frac{1}{10} = 9$

mmol of NaOH left = $9 - 1 = 8$

Since base is left, ∴ pH > 7

(3) mmol of HCl = $55 \times \frac{1}{10} = 5.5$

mmol of NaOH = $45 \times \frac{1}{10} = 4.5$

mmol of HCl left = $5.5 - 4.5 = 1.0$

Volume = $55 + 45 = 100$

$$[H^{\oplus}] = \frac{1}{100} = 10^{-2}$$

pH = 2

(4) mmol of HCl = $100 \times \frac{1}{10} = 10$

mmol of NaOH = $100 \times \frac{1}{10} = 10$

Both S_A and S_B are neutralised.

∴ pH = 7

4. **(1)** pH = 6 ∴ $[H^{\oplus}] = 10^{-6}$ M.

Volume is made 100 times.

$$\therefore [H^{\oplus}] = \frac{10^{-6}}{100} = 10^{-8} \text{ M}$$

pH = 6.95

5. **(2)** pH = 13

$[H^{\oplus}] = 10^{-13}\text{ M} = 10^{-13}\text{ mol } (1000\text{ mL})^{-1}$

$$= \frac{10^{-13}}{1000} = 10^{-16} \text{ mol mL}^{-1}$$

Number of $[H^{\oplus}] = 10^{-16} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{7}$ ions

6. **(2)** pH = 1, $[H^{\oplus}] = 10^{-1}$ M

pH = 5 $[H^{\oplus}] = 10^{-5}$ M

Volume becomes double

$$[H^{\oplus}]_{\text{Final}} = \frac{(10^{-1} + 10^{-5})}{2} \quad (10^{-5} \text{ is negligible})$$

$$= \frac{1}{2} \times 10^{-1} = 0.5 \times 10^{-1} = 5 \times 10^{-2}$$

$\text{pH} = -\log(5 \times 10^{-2})$

$= -\log 0.7 + 2 = 1.3$

The pH is between 1 and 2.

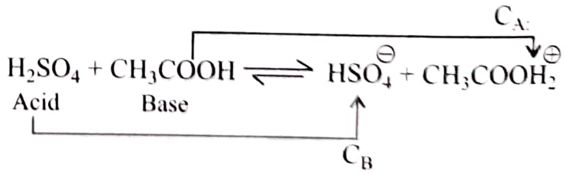
7. **(1)** With increase in temperature the ionisation of H_2O increases and hence the $[H^{\oplus}]$ and $[\overset{\ominus}{O}H]$ increases. Therefore, pH and pOH decreases with increase of temperature.

8. **(1)** pH = 3, $[H^{\oplus}] = 10^{-3}$

pH = 6, $[H^{\oplus}] = 10^{-6}$

$[H^{\oplus}]$ decreases, which is only possible if the solution is diluted to 1000 times, i.e.,

9. **(3)** $[H^{\oplus}] = \frac{10^{-3}}{1000} = 16^{-6} \Rightarrow \text{pH} = 6$



$$H_2SO_4 + CH_3COOH \rightleftharpoons HSO_4^{\ominus} + CH_3COOH_2^{\oplus}$$

Conjugate acid are = $(CH_3CO\overset{\oplus}{O}H_2, H_2SO_4)$

Conjugate base are ∴ $(HSO_4^{\ominus}, CH_3COOH)$

Hence answer is (3).

10. **(1)** Atmospheric species are those which can loose a proton and can accept a proton.

(1) $H_3O^{\oplus} \underset{+H^{\oplus}}{\rightleftharpoons} H_2O \underset{-H^{\oplus}}{\rightleftharpoons} \overset{\ominus}{O}H + H^{\oplus}$

$$H_3PO_3 \underset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Dibasic}\\ \text{acid}}}{H_2PO_3^{\ominus}} \underset{-H^{\oplus}}{\rightleftharpoons} HPO_3^{2-} + H^{\oplus}$$

$$H_2PO_4^{\ominus} \underset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Tribasic}\\ \text{acid.}}}{HPO_4^{2-}} \underset{-H^{\oplus}}{\rightleftharpoons} PO_4^{3-} + H^{\oplus}$$

(2) $$H_2C_2O_4 \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Dibasic}\\ \text{acid.}}}{HC_2O_4^{\ominus}} \overset{-H^{\oplus}}{\rightleftharpoons} C_2O_2^{2-} + H^{\oplus}$$

$$H_3PO_4 \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Tribasic}\\ \text{acid.}}}{H_2PO_4^{\ominus}} \overset{-H^{\oplus}}{\rightleftharpoons} HPO_4^{2-} + H^{\oplus}$$

$$HSO_4^{\ominus} \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Monobasic}\\ \text{acid.}}}{SO_4^{2-}} \longrightarrow \begin{matrix}\text{Cannot loose}\\ \text{proton}\end{matrix}$$

(3) $$H_3O^{\oplus} \overset{+H^{\oplus}}{\rightleftharpoons} H_2O \overset{-H^{\oplus}}{\rightleftharpoons} \overset{\ominus}{O}H + H^{\oplus}$$

$$H_2PO_4^{\ominus} \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\text{Tribasic acid}}{HPO_4^{2-}} \overset{-H^{\oplus}}{\rightleftharpoons} PO_4^{3-} + H^{\oplus}$$

$$H_3PO_2^{\ominus} \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\text{Monobasic acid}}{H_2PO_2^{\ominus}} \longrightarrow \begin{matrix}\text{Cannot loss}\\ \text{proton}\end{matrix}$$

(4) $$\begin{matrix}\text{Cannot}\\ \text{accept proton}\end{matrix} \longleftarrow H_3O^{\oplus} \overset{-H^{\oplus}}{\rightleftharpoons} H_2O + H^{\oplus}$$

$$H_3PO_4 \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Tribasic}\\ \text{acid.}}}{H_2PO_4^{\ominus}} \overset{-H^{\oplus}}{\rightleftharpoons} HPO_4^{2-} + H^{\oplus}$$

$$H_2CO_3 \overset{+H^{\oplus}}{\rightleftharpoons} \underset{\substack{\text{Dibasic}\\ \text{acid.}}}{HCO_3^{\ominus}} \overset{-H^{\oplus}}{\rightleftharpoons} CO_3^{2-} + H^{\oplus}$$

Hence answer is (1).

11. **(4) NaCl (aq):**

Reduction potention of H_2O > reduction potential of $Na^{\oplus}$ ion.

Hence water undergoes reduction to give $H_2(g)$ and $\overset{\ominus}{O}H$ ions at calhode.

Cathode ⇒ $H_2O + e^- \longrightarrow \overset{\ominus}{O}H + \frac{1}{2}H_2$

So solution becomes basic

Anode ⇒ $Cl^{\ominus} \longrightarrow \frac{1}{2}Cl_2 + e^-$

1 F = 1 Eq of $\overset{\ominus}{O}H$

Number of Faraday's $= \dfrac{9650}{96500} = 0.1$

$\overset{\ominus}{O}H = 0.1$ Eq or 0.1 mol

$V_{sol} = 1$ L

$[\overset{\ominus}{O}H] = \dfrac{0.1\text{ Eq}}{1\text{ L}} = 0.1$ N or M

$pOH = -\log(10^{-1}) = 1$

$pH = 14 - 1 = 13$

12. **(2)** mmol of NaOH = 200 × 0.0657 = 13.14

mmol of HCl = 140 × 0.107 = 14.98

mmol of HCl left = 14.98 − 13.14 = 1.84

Total volume = (200 + 140 + 160) mL = 500 mL

$$[H^{\oplus}] = \frac{1.84\text{ m mol.}}{500\text{ mL}} = 0.00368 = 368 \times 10^{-5}$$

$$pH = -\log(368 \times 10^{-5}) = -2.5658 + 5$$
$$= 2.4342 \approx 2.43$$

$pH = 2.43$

13. **(4)** When pH = 7, $[H^{\oplus}]$ initial $= 10^{-7}$ M

When pH = 4, $[H^{\oplus}]$ Total $= 10^{-4}$ M

∴ $[H^{\oplus}]$ added from HCl $= (10^{-4} - 10^{-7})$

$= 10^{-4}(1 - 0.001) \approx 10^{-4}$ M

When another drop of HCl is added:

When pH = 4, $[H^{\oplus}]$ initial $= 10^{-4}$ M

∴ $[H^{\oplus}]$ added $\approx 10^{-4}$

$[H^{\oplus}]$ Total $= (10^{-4} + 10^{-4}) = 2 \times 10^{-4}$ M

∴ $pH = -\log(2 \times 10^{-4}) = -0.3 + 4 = 3.7$

Note: Change in volume on adding one drop of HCl is assumed to be negligible.

Exercise 8.2

1. **(3)** $K_w = [H^{\oplus}][\overset{\ominus}{O}H] = 10^{-6} \times 10^{-6} = 10^{-12}$

2. **(1)** Since pH is same for two acids.

∴ $[H^{\oplus}]_1 = [H^{\oplus}]_2$

Thus, $C_1\alpha_1 = C_2\alpha_2$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{C_1\alpha_1^2}{C_1\alpha_2^2} = \frac{\alpha_1}{\alpha_2} \quad \text{...}(i)$$

$$\alpha_1 = \sqrt{\frac{K_{a_1}}{C_1}}, \qquad \alpha_2 = \sqrt{\frac{K_{a_2}}{C_2}}$$

$$\therefore \quad \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}C_2}{K_{a_2}C_1}}$$

Substituting from equation (i) the value of α_1/α_2

$$\frac{K_{a_1}}{K_{a_2}} = \sqrt{\frac{K_{a_1}C_2}{K_{a_2}C_1}}$$

$$\therefore \quad \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

$$4 = \frac{C_2}{C_1}$$

$$\therefore \quad C_1 : C_2 = \frac{1}{4} = 0.25$$

3. **(4)** $K_a = \dfrac{[H^{\oplus}][\overset{\ominus}{O}H]}{[H_2O]} = \dfrac{K_w}{[H_2O]} = \dfrac{10^{-14}}{55.6} = 18 \times 10^{-17}$

(M of H_2O = 55.6)

4. (1) Statement (*a*) is wrong since it is not valid at all temperature.

5. (3)

$$\begin{array}{cccc} A_xB_y & \rightleftharpoons & xA^{+y} & + & yB^{-x} \\ 1 & & 0 & & 0 \\ C(1-\alpha) & & x\cdot C\alpha & & y\cdot C\alpha \end{array}$$

$$K_a = \frac{(x\cdot C\alpha)^x\,(y\cdot C\alpha)^y}{C(1-\alpha)}$$

(Assuming $1-\alpha \approx 1$)

$$K_a = \frac{x^x\cdot y^y\cdot C^{x+y}\cdot\alpha^{x+y}}{C}$$

$$K_a = x^x y^y\cdot C^{x+y-1}\cdot\alpha^{x+y}$$

$$\therefore \quad \alpha^{x+y} = \frac{K_a}{x^x\cdot y^y\cdot C^{x+y-1}}$$

$$\therefore \quad \alpha = \left(\frac{K_a}{x^x\cdot y^y\cdot C^{x+y-1}}\right)^{\frac{1}{x+y}}$$

6. (3) $K_b = 1.8\times10^{-5}$

$pK_b = 4.7447$

$$pOH_{W_B} = \frac{1}{2}(pK_b - \log 0.1)$$

$$= \frac{1}{2}(4.7447+1) = 2.87.$$

$$[\overset{\ominus}{O}H] = \text{Antilog}(-2.87)$$

$= \text{Anitilog}(-2-0.87+1-1)$

$= \text{Antilog}\ (\bar{3}.13)$

$= 1.34\times10^{-3}$

7. (1) Higher the K_a value, stronger is the acid and high concentration of $H^{\oplus}$ ions and low pH value.

Thus, the order of pH is:

$D > C > B > A.$

8. (3) $pK_b = 4.7447 \approx 4.74$

pH = 12, pOH = 2

$$pOH = \frac{1}{2}(pK_b - \log C)$$

$2\times2 = pK_b - \log C$

$4 = 4.74 - \log C$

$\therefore\ \log C = 0.74$

$C = \text{Antilog}(0.74) = 0.55$ M

9. (2) $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.1}} = 10^{-2}$

$\alpha\% = 10^{-2}\times100 = 1\%$

10. (3) For any polyprotic acid H_3A, the successive dissociation constants reduces as $K_1 >> K_2 >> K_3$.

11. (2) Add two equations to get :

$K_a\times K_b = K_w$

12. (4) $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

$HA + NaOH \longrightarrow NaA + H_2O$

or

$$HA + \overset{\ominus}{O}H \longrightarrow A^{\ominus} + H_2O$$

$$K_{Eq} = \frac{[A^{\ominus}][H_2O]}{[HA][\overset{\ominus}{O}H]}$$

$$\frac{K_{eq}}{K_a} = \frac{1}{[H^{\oplus}][\overset{\ominus}{O}H]} = \frac{1}{K_w}$$

$$\therefore\ K_{eq} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

13. (4) 10^{-8} M HCl:

(1) $[H^{\oplus}] = 10^{-8} = 10\times10^{-9}$

(if dissociation of water is neglected)

(2) If dissociation of water is not neglected:

$$\begin{array}{ccccc} H_2O & \rightleftharpoons & H^{\oplus} & + & \overset{\ominus}{O}H \\ & & a+10^{-8} & & a \end{array}$$

$a(a+10^{-8}) = 10^{-14}$

$a = 0.95\times10^{-7}$

$\therefore$ % error =

$$= \left(\frac{10\times10^{-9} - 9.5\times10^{-9}}{10\times10^{-9}}\right)\times100 = 5\%$$

14. (1) $H_3BO_3 + \overset{\ominus}{O}H \longrightarrow B(OH)_4^{\ominus} + H^{\oplus}$

H_3BO_3 is a monobasic acid. It accept lone pair of electrons and thus acts as weak Lewis acid.

15. (3) $H_2S + \overset{\ominus}{O}H \longrightarrow H_2O + HS^{\ominus}$ $\qquad \Delta H_1 = -37.1$ kJ

$H^{\oplus} + \overset{\ominus}{O}H \longrightarrow H_2O$ $\qquad \Delta H_2 = -57.1$ kJ

(ΔH_2 is the heat of neutralisation of S_A and S_B).

$\therefore\ H_2S \rightleftharpoons HS^{\ominus} + H^{\oplus}$ $\qquad (\Delta H = ?)$

$\Delta H = \Delta H_1 - \Delta H_2$

$= -37.1 - (-57.1) = 20.0$ kJ

16. (2) $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$

For W_A :

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4\times10^{-5}}{0.1}} = 2\times10^{-2}$$

When HCl is added, due to common ion ($H^{\oplus}$ ion), suppression of ionisation of HA occurs.

Total volume = 200 + 100 = 300 mL

$M_1V_2 = M_2V_2$ (for HCl)

$100\times0.2 = M_2\times300$

$$M_2 = \frac{0.2}{3}$$

$$\alpha' = \frac{K_a}{M}$$

(M = Concentration of common ion added)

$$\therefore\ \alpha' = \frac{4\times10^{-5}}{0.2/3} = 6\times10^{-4}$$

Change in α (factor) :

$$\frac{\alpha'}{\alpha} = \frac{6\times10^{-4}}{2\times10^{-2}} = 0.03$$

17. (3) 88 ppm means:

10^6 mL of air contains = 88 of CO_2

$$= \frac{88}{44} = 2 \text{ mol } CO_2$$

Moles of CO_2 is 10^5 mL = $\frac{2}{10^6}\times10^5 = 0.2$ mol

$$[CO_2] = \frac{0.2 \text{ mol}}{1 \text{ dm}^3} = 0.2 \text{ M}$$

For H_2CO_3, consider only first dissociation constant (K_{a_1}) to calculate pH of solution.

$$H_2CO_3 \rightleftharpoons H^\oplus + HCO_3^\ominus$$

$$[H^\oplus] = \sqrt{K_{a_1}C} = \sqrt{10^{-7}\times0.2} = \sqrt{2}\times10^{-4}$$

$$pH = -\log 2^{\frac{1}{2}} + 4$$

$$= -\frac{1}{2}\times0.3+4 = 3.85$$

$$pOH = 14 - 3.85 = 10.15$$

18. (1) $K_a = \frac{C\alpha^2}{(1-\alpha)}$

For 1% error : $\alpha = 0.01$

$$K_a = \frac{C(0.01)^2}{(1-0.01)} = \frac{C\times10^{-4}}{0.99}$$

$$C \Rightarrow \frac{K_a\times0.99}{10^{-4}}$$

$$\Rightarrow 9900\, K_a$$

19. (1) Let α and α′ are the degree of ionisation of HX and HY at same concentration.

$$\begin{array}{cccc} HX & \rightleftharpoons H^\oplus & + & X^\ominus \\ 1-\alpha & (\alpha+\alpha') & & \alpha \\ HY & \rightleftharpoons H^\oplus & + & Y^\ominus \\ (1-\alpha') & (\alpha+\alpha') & & \alpha' \end{array}$$

$$K_{HY} = \frac{[\alpha][\alpha+\alpha']C}{[1-\alpha]}$$

$$K_{HY} = \frac{[\alpha'][\alpha+\alpha']C}{[1-\alpha']}$$

$$\therefore \quad \frac{K_{HX}}{K_{HY}} = \left[\frac{\alpha}{1-\alpha}\right]\times\left[\frac{1-\alpha'}{\alpha'}\right]$$

$$\left(\frac{\alpha}{1-\alpha}\right) = \frac{1.75\times10^{-5}}{1.3\times10^{-5}}\times\left[\frac{\alpha'}{1-\alpha'}\right]$$

The ratio is unrelated to molarity, pH and K_a.

20. (3) Refer to illustration 8.47.

$$H_2S \rightleftharpoons H^\oplus + HS^\ominus \; (K_1)$$

$$HS^\ominus \rightleftharpoons H^\oplus + S^{2-} \; (K_2)$$

$$K_1 = \frac{[H^\oplus][HS^\ominus]}{[H_2S]}$$

$$K_2 = \frac{[H^\oplus][S^\ominus]}{[HS^\ominus]}$$

$$K_1\times K_2 = \frac{[H^\oplus]^2[S^{2-}]}{[H_2S]}$$

$$[H^\oplus]^2 = \frac{K_1\times K_2\times[H_2S]}{[S^{2-}]}$$

Taking negative logarithms to both sides.

$$-2\log[H^\oplus] = -\log K_1 - \log K_2$$

$$= -\log[H_2S] + \log[S^{2-}]$$

$$\therefore \; pH = \frac{1}{2}\left(pK_1 + pK_2 + \log\frac{[S^{2-}]}{[H_2S]}\right)$$

Exercise 8.3

1. (4) (1) Mixture of salt of $S_A/S_B + S_B$.
   (2) Salt of W_A/W_B.
   (3) Mixture of salt of $S_A/S_B + W_B$.
   (4) Mixture of salt of $W_A/S_B + W_A$ (Buffer)
2. (1) Mixture of $W_B + W_A$. (not buffer)
   (2), (3), and (4) are mixture of W_A + Salt of W_A/S_B (Buffer)
3. (3) Rule (AAA): In acid buffer (A), on addition of S_A(A), the concentration of W_A(A) increases and that of salt decreases, so pH decreases.

$$pH = pK_a + \log\frac{[\text{Salt} - x]}{[\text{Acid} + x]}$$

(x is the concentration of H_2SO_4 added)

4. (2) Maximum buffer capacity, when pH = pK_a, and this is only possible when [Salt] = [Acid].
5. (2) $pH = pK_a + \log\frac{[A^\ominus]}{[HA]}$

$$5 = 6 + \log\frac{[A^\ominus]}{[HA]}$$

$$\therefore \quad \log\frac{[HA]}{[A^\ominus]} = 1$$

$$\therefore \quad \frac{[HA]}{[A^\ominus]} = \text{Antilog}(1) = 10.$$

6. (2) On adding salt of W_A/S_B (NaH_2PO_4) to 0.1 M H_3PO_4, an acidic buffer is formed so pH increases.
7. (3) On dilution, the concentration of both salt and acid decreases, so the $\frac{[\text{Salt}]}{[\text{Acid}]}$ remains same and pH does not change.
8. (1)

	CH_3COOH	$+ NaOH$	$\longrightarrow CH_3COONa$	$+ H_2O$
Initial mol	0.1	0.05	0	0
Final mol	(0.1 – 0.05) = 0.05	(0.05 – 0.05) = 0	0.05	–

Total moles of $CH_3COONa = 0.2 + 0.05 = 0.25$.

$$\therefore\ [CH_3COONa] = \frac{0.25\ \text{mol}}{1\ \text{L}} = 0.25\ \text{M}$$

Moles of CH_3COOH left $= (0.1 - 0.05) = 0.05$

$$\therefore\ [CH_3COOH] = \frac{0.05\ \text{mol}}{1\ \text{L}} = 0.05\ \text{M}$$

Thus, acidic buffer is formed

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.74 + \log\left(\frac{0.25}{0.05}\right)$$

$$= 4.74 + \log 5 = 4.74 + 0.7 = 5.44.$$

9. (4) $\underset{W_B}{\text{BOH}} + \underset{S_A}{\text{HA}} \longrightarrow \underset{(\text{Salt of } W_B/S_A)}{\text{BA}} + H_2O.$

$\left[W_B \text{ is in excess, so basic buffer is formed}\right]$

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{BA}]}{[\text{BOH}]}$$

$(\text{pH} = 9,\ \text{pOH} = 14 - 9 = 5)$

$$5 = \text{p}K_b + \log\left(\frac{10}{V - 10}\right) \quad \text{...(i)}$$

When pH = 8, $\therefore$ pOH = 14 – 8 = 6.

$$6 = \text{p}K_b + \log\left(\frac{25}{V - 25}\right)$$

Solve equation (i) and (ii),

$V = 30$ mL.

10. (3) Rule (BBB): In basic buffer (B), on addition of $S_B(B)$, the concentration of $S_B(B)$ increases and that of salt decreases.

$$\text{pOH}_{\text{initial}} = \text{p}K_b + \log\frac{[NH_4Cl]}{[NH_3]}$$

$$\text{pOH}_{\text{initial}} = 4.74 + \log\frac{0.1}{0.1}$$

$\therefore\ \text{pOH}_{\text{initial}} = 4.74.$

On adding 0.05 M NaOH:

$[NH_4Cl] = 0.1 - 0.05 = 0.05$ M

$[NH_3] = 0.1 + 0.05 = 0.15$ M

$$\text{pOH}_{\text{final}} = \text{p}K_b + \log\frac{0.05}{0.15}$$

$$= \text{p}K_b - \log 3$$

$$= 4.74 - 0.48 = 4.26$$

Change in pOH (ΔpOH) $= \text{pOH}_f - \text{pOH}_i$

$= 4.26 - 4.74 = -0.48$

Change in pH = –(change is pOH)

$= -(-0.48) = 0.48$

11. (1) $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$

$$K_1 = \frac{[H^{\oplus}][HCO_3^{\ominus}]}{[H_2CO_3]} = \frac{[H^{\oplus}][HCO_3^{\ominus}]}{[CO_2]}$$

$$\frac{K_1}{[H^{\oplus}]} = \frac{[HCO_3^{\ominus}]}{[CO_2]} = \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$\text{pH} = 7.4,\ \log[H^{\oplus}] = -7 - 0.4 + 1 - 1 = \bar{8}.6$

$\therefore\ [H^{\oplus}] = \text{Antilog}\ (\bar{8}.6) = 4 \times 10^{-8}$

$$\therefore\ \frac{[HCO_3^{\ominus}]}{[CO_2]} = \frac{K_1}{[H^{\oplus}]} = \frac{4.5 \times 10^{-7}}{4 \times 10^{-8}} = 11.25$$

12. (3) Blood is basic with pH = 7.4.

13. (4) Self explanatory.

14. (4) $\text{p}K_a = -\log(5 \times 10^{-10})$

$= -0.7 + 10 = 9.3$

Acidic buffer will be formed.

$$\text{pH} = \text{p}K_a + \log\frac{[KCN]}{[HCN]} \quad \text{...(i)}$$

Let V mL of KCN is added

Total volume = $(V + 10)$ mL

mmol of KCN = $5 \times V$

$$\therefore\ [KCN] = \frac{5 \times V\ \text{mmol}}{(V + 10)\ \text{mL}}$$

mmol of HCN = $2 \times 10 = 20$

$$\therefore\ [HCN] = \frac{20\ \text{mmol}}{(V + 10)\ \text{mL}}$$

Thus, from equation (i),

$$9 = 9.3 + \log\left[\frac{5V/(V + 10)}{20/(V + 10)}\right]$$

$$-0.3 = \log\left(\frac{5V}{20}\right)$$

$$\log\left(\frac{V}{4}\right) = -0.3$$

$$\frac{V}{4} = \text{Antilog}(-0.3 + 1 - 1)$$

$= \text{Antilog}(\bar{1}.7) = 5 \times 10^{-1}$

$V = 20 \times 10^{-1} = 2$ mL

15. (4) For neutralisation of CH_3COOH with NaOH:

mmol of CH_3COOH = mmol of NaOH

$= 6 \times 0.1 = 0.6$

For neutralisation CH_3COONa with HCl:

mmol of CH_3COONa = mmol of HCl

$= 12 \times 0.1 = 1.2$

Concentration of acid and salt in 18 mL of mixture:

$$[CH_3COOH] = \frac{0.6\ \text{mmol}}{18\ \text{mL}}$$

$$[CH_3COONa] = \frac{1.2\ \text{mmol}}{18\ \text{mL}}$$

$$\text{pH} = 4.75 + \log\left(\frac{1.2}{0.6}\right)$$

$= 4.75 + \log 2 = 4.75 + 0.3 = 5.05$

16. (1) $H_2O + CO_2 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$

If CO_2 is increased, according to Le Chatelier's principle, $[H^{\oplus}]$ will increase, thereby pH will decrease.

Body very minutely maintains pH of the blood. The lungs will work faster so as to exhale the excess of CO_2 and maintains its pH again at 7.4.

17. (1) Let V mL of acid solution is taken.

mmol of acid $= 0.1 \times V$.

mmol of salt $= 0.2\text{ M} \times (300 - V)$ mL

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$3.9 = 4.2 + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$-0.3 = \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\log\frac{[\text{Acid}]}{[\text{Salt}]} = 0.3$$

$$\frac{[\text{Acid}]}{[\text{Salt}]} = \text{Antilog}(0.3) = 2$$

$$\therefore\ [\text{Acid}] = 2[\text{Salt}]$$

$$\frac{0.1 \times V}{\cancel{300}} = 2 \times \left[\frac{0.2 \times (300 - V)}{\cancel{300}}\right]$$

Solve for V:

$V = 240$ mL

18. (1)

$$\begin{array}{lccccc} & \text{RNH}_2 & + & \text{HCl} & \longrightarrow & \overset{\oplus}{\text{RNH}_3} + \text{Cl}^{\ominus} \\ \text{Initial mol} & 0.1 & & 0.08 & & 0 \qquad 0 \\ \text{Final moles} & (0.1 - 0.08) & & (0.08 - 0.08) & & 0.08 \qquad - \\ & = 0.02 & & = 0 & & \end{array}$$

W_B is left behind so basic buffer is formed.

Use Henderson's equation :

$$[\overset{\ominus}{\text{OH}}] = K_b\frac{[\text{Base}]}{[\text{Salt}]}$$

$$= 5 \times 10^{-14} \times \frac{0.02}{0.08} = 1.25 \times 10^{-4}.$$

$$\therefore\ [\text{H}^{\oplus}] = \frac{K_w}{[\overset{\ominus}{\text{OH}}]} = \frac{10^{-14}}{1.25 \times 10^{-4}}$$

$$= 8 \times 10^{-11}\text{ M}$$

19. (2) Salt of W_A/S_B is formed.

$$\begin{array}{ccccc} \text{X}^{\ominus} + \text{H}_2\text{O} & \rightleftharpoons & \text{HX} & + & \overset{\ominus}{\text{OH}} \\ 1 \qquad - & & 0 & & 0 \\ C(1-h) & & Ch & & Ch \end{array}$$

$$\therefore\ h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}}$$

$$= \left(\frac{10^{-14}}{10^{-5} \times 0.1}\right)^{1/2} = 10^{-4}$$

$\% h = 10^{-4} \times 100 = 10^{-2} = 0.01$

20. (3) NaCl (Salt of S_A/S_B): pH = 7

NaCN (Salt of W_A/S_B): pH > 7

HCl (S_A): pH << 7

NH_4Cl (Salt of S_A/W_B): pH < 7.

Hence the order is (c).

NaCN > NaCl > NH_4Cl > HCl

21. (2) For the salt of W_A/W_B, the degree of hydrolysis is independent of concentration.

22. (1) Lower pH means higher K_a value and thus stronger is the acid.

23. (2) Salt of W_B/S_A have pH < 7.

(Salt of W_A/W_B have pH < 7, if acidic part is stronger, i.e., if $K_a > K_b$ or $\text{p}K_b > \text{p}K_a$)

(1) Salt of $Ba(OH)_2(S_B)$ HI (S_A)

$\therefore$ pH = 7

(2) Salt of $Al(OH)_3$ (S_B) and HNO_3 (S_A)

$\therefore$ pH < 7.

(3) Salt of CH_3COOH (W_A) and NH_4OH (W_B) (but $K_a = K_b$), so pH = 7.

(4) Salt of Cs(OH) (S_B) and HI (S_A) so pH = 7.

24. (4) Salt of S_B/S_A have pH > 7.

(Salt of W_A/W_B have pH > 7, if basic is stronger, i.e., if $K_b > K_a$ or $\text{p}K_a > \text{p}K_b$).

$$\begin{array}{llccc} \textbf{I.} & \text{BaF}_2 & \equiv \text{Ba(OH)}_2 & + & \text{HF} \\ & \text{Salt of } S_B/S_A & S_B & & W_A \\ & (\text{pH} > 7) & & & \\ \textbf{II.} & \text{RbI} & \equiv \text{RbOH} & + & \text{HI} \\ & \text{Salt of } S_B/S_A & S_B & & S_A \\ & (\text{pH} = 7) & & & \\ \textbf{III.} & \text{C}_6\text{H}_5\text{COONa} & \equiv \text{C}_6\text{H}_5\text{COOH} & + & \text{NaOH} \\ & \text{Salt of } W_A/S_B & W_A & & S_B \\ & (\text{pH} > 7) & & & \\ \textbf{IV.} & (\text{CH}_3\text{COO})_2\text{Ca} & \equiv 2\text{CH}_3\text{COOH} & + & \text{Ca(OH)}_2 \\ & \text{Salt of } W_A/S_B & W_A & & S_B \\ & (\text{pH} > 7) & & & \end{array}$$

25. (4) pH of salt of W_A/S_B is

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C)$$

$$= \frac{14}{2} + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}\text{p}K_a(\text{CH}_3\text{COOH}) + \frac{1}{2}\log[\text{Salt}]$$

26. (2) Higher $[H_3O^{\oplus}]$, lower is the pH.

$H_2SO_4 \equiv S_A \Rightarrow$ Highest $[H_3O^{\oplus}]$

$H_2S \equiv W_A \Rightarrow$ Lower $[H_3O^{\oplus}]$

NaCl and $NaNO_3 \equiv$ Salt of S_A/S_B (pH = 7)

$\Rightarrow$ Lowest $[H_3O^{\oplus}] = 10^{-7}$ M

Hence, the order is (2).

27. (4) pH = 11 shows that Y is salt of W_A/S_B (pH > 7).

28. (1) $K_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$

29. (4) pH of salt of W_A/S_B is basic (pH > 7)

(1) Salt of W_A/W_B

(2) Salt of W_B/S_A

(3) Salt of W_B/S_A

(4) Salt of W_A/S_B

30. (3) $\text{ASc}^{\ominus} + H_2O \rightleftharpoons \text{HASc} + \overset{\ominus}{\text{OH}}$

$$[\overset{\ominus}{\text{OH}}] = Ch = C\sqrt{\left(\frac{Kh}{C}\right)} = \sqrt{K_h C}$$

$$= \sqrt{\frac{K_w \cdot C}{K_a}} = \left(\frac{10^{-14} \times 0.02}{5 \times 10^{-5}}\right)^{\frac{1}{2}}$$

$$= 2 \times 10^{-6}\ \text{M}$$

$$[H_3O^{\oplus}] = \frac{K_w}{[\overset{\ominus}{O}H]} = \frac{10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9}$$

Exercise 8.4

1. **(1) 2. (2)** 3. **(4)** (All self explanatory)

4. **(3)** Refer illustration 8.92.

5. **(1)** Titration of W_B/S_A. pH at equivalence point is ≈ 5.5.

6. **(3)** (W_A or W_B)

7. **(2)** Titration of W_A/S_B. pH at equivalence point is > 8.

8. **(3)** 9. **(4)**

Solubility and K_{sp}:

10. **(1)** Q_{sp} or IP $= [Ca^{2+}]\ [F^{\ominus}]^2$ (Volume is doubled and concentration is halved)

$$= \left(\frac{10^{-2}}{2}\right)\left(\frac{10^{-3}}{2}\right)^2 = \frac{1}{8} \times 10^{-8} = 0.125 \times 10^{-8}$$

$$= 1.25 \times 10^{-9}.$$

$Q_{sp} > K_{sp}$ $(1.25 \times 10^{-9} > 1.7 \times 10^{-10})$

Hence, precipitate of CaF_2 will occur.

$$(2)\ Q_{sp} < K_{sp} \left[\left(\frac{10^{-4}}{2}\right) \times \left(\frac{10^{-4}}{2}\right)^2 = 1.25 \times 10^{-13}\right]$$

$$(3)\ Q_{sp} < K_{sp} \left[\left(\frac{10^{-3}}{2}\right) \times \left(\frac{10^{-5}}{2}\right)^2 = 1.25 \times 10^{-14}\right]$$

$$(4)\ Q_{sp} < K_{sp} \left[\left(\frac{10^{-5}}{2}\right) \times \left(\frac{10^{-3}}{2}\right)^2 = 1.25 \times 10^{-13}\right]$$

[No precipitation] in (2), (3), and (4).

11. **(4)** $K_{sp} = (2)^2 \cdot (3)^2 \cdot x^{2+3} = 108x^5$

12. **(2)** pH = 10.6, pOH = 14 – 10.6 = 3.4

$$\therefore\ [\overset{\ominus}{O}H] = \text{Antilog}(-3.4)$$
$$= \text{Antilog}(-3 - 0.4 + 1 - 1)$$
$$= \text{Antilog}(\bar{4}.6)$$
$$= 4 \times 10^{-4}\ \text{M}$$

$$\therefore\ [Ca(OH)_2 \rightarrow \underset{S}{Ca^{2+}} + \underset{2S\, =\, 4 \times 10^{-4}\ \text{M}}{2\overset{\ominus}{O}H}](K_{sp}[Ca^{2+}][\overset{\ominus}{O}H]^2)$$

$$\therefore\ [Ca^{2+}] = \frac{4 \times 10^{-4}}{2}\ \text{M}$$

$$= \left(\frac{4 \times 10^{-4}}{2}\right)(4 \times 10^{-4})^2$$

$$= 32 \times 10^{-12} = 3.2 \times 10^{-11}\ \text{M}^3$$

$$K_{sp} = [Ca^{2+}]\ [\overset{\ominus}{O}H]^2$$

13. **(4)** $\text{AgI} \rightleftharpoons \underset{x}{Ag^{\oplus}} + \underset{x}{I^{\ominus}}\ \Big]\ K_{sp} = [Ag^{\oplus}][I^{\ominus}]$

$$\therefore\ [I^{\ominus}] = (x + 0.1)$$

$$\begin{array}{ccccc} BaI_2 & \rightleftharpoons & Ba^{2+} & + & 2I^{-} \\ 0.005\ \text{M} & & 0 & & 0 \\ 0 & & 0.05\ \text{M} & & 2 \times 0.05 = 0.1\ \text{M} \end{array}$$

$$\therefore\ [I^{\ominus}] = (x + 0.1)$$

$$K_{sp} = [Ag^{\oplus}]\ [I^{\ominus}] = x(x + 0.1)$$
$$= x^2 + 0.1x \approx 0.1x\ (\text{neglecting } x^2)$$
$$= 0.1 \times 10^{-15} = 10^{-16}.$$

Solubility of AgI in pure water.

$$= \sqrt{K_{sp}} = \sqrt{10^{-16}} = 10^{-8}\ \text{M}$$

14. **(4)** $\ln S$ vs $\frac{1}{T}$ graph with negative slope.

$\therefore\ \Delta H > 0 \Rightarrow$ Salts with water of crystallisation.

i.e., $CuSO_4 \cdot 5H_2O$

15. **(3)** $CaF_2 \rightleftharpoons Ca^{2+} + 2F^{\ominus}$

(Let S is the solubility of CaF_2 in H_2O)?

$$\therefore\ [Ca^{2+}] \text{ in } H_2O = S,\ [F^{\ominus}]_{H_2O} = 2S$$

$$[Ca^{2+}] \text{ in } 0.1\ \text{M}\ Ca(NO_3)_2 = S - 0.1$$
$$[F^{\ominus}] \text{ in } 0.1\ \text{M}\ Ca(NO_3)_2 = 2S$$

$$\therefore\ 2S = [F^{\ominus}]_{\text{in } H_2O}$$

$$S = \frac{[F^{\ominus}]}{2}$$

16. **(3)** $S = (K_{sp})^{1/2} = (1.44 \times 10^{-8})^{1/2}$

$$= 12 \times 10^{-5}$$
$$= 303 \times 12 \times 10^{-5}\ \text{g L}^{-1}$$
$$= 3636 \times 10^{-5}\ \text{g L}^{-1}$$
$$= 0.03636\ \text{g L}^{-1} = 0.03636\ \text{mg mL}^{-1}$$

$$V_{H_2O} = \frac{1}{0.03636} = \frac{10^5}{3636} = 27.5\ \text{mL}$$

17. **(3)** $S_{AgCl} = \sqrt{K_{sp}} = (2 \times 10^{-10})^{1/2}$

$$= 1.414 \times 10^{-5}\ \text{M}$$

$$S_{AgBr} = \sqrt{K_{sp}} = (5 \times 10^{-13})^{1/2}$$
$$= (50 \times 10^{-14})^{1/2} = 7.071 \times 10^{-7}\ \text{M}$$

$$S_{Ag_2CrO_4} = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{2.4 \times 10^{-12}}{4}\right)^{1/3}$$

$$= (0.6)^{1/3} \times 10^{-4}$$

$$= (6)^{1/3} \times \left(\frac{1}{10}\right)^{1/3} \times 10^{-4}$$

$$= 1.817 \times \frac{1}{2.154} \times 10^{-4}$$

$$= 0.8 \times 10^{-4} = 8 \times 10^{-5}\ \text{M}$$

Solubility of Ag_2CrO_4 is maximum.

Note : Don't solve the exact value, take an approximation of cube root of 10^{-12} to get the approximate answer).

So solubility is maximum in Ag_2CrO_4.

18. (1) Let x g of KBr.

$$\text{Moles of KBr} = \frac{x}{120},\ M = \frac{x}{120 \times 1\,\text{L}}$$

$$\therefore\ [Ag^{\oplus}] = [AgNO_3] = 0.12\text{ M}$$

$$[Br^{\ominus}] = [KBr] = \frac{x}{120}$$

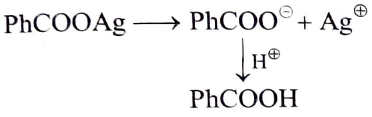
When the precipitation just starts, $Q_{sp} = K_{sp}$

$$[Ag^{\oplus}]\,[Br^{\ominus}] = 10^{-13}$$

$$0.12 \times \frac{x}{120} = 10^{-13}$$

$$\therefore\ x = 10^{-10}\text{ g}$$

19. (3) The solubility of salt of W_A increases with increase in concentration of $H^{\oplus}$ or at lower pH value due to the protonation of anion, which increases the ionisation of the salt.



$$\begin{array}{c} PhCOOAg \longrightarrow PhCOO^{\ominus} + Ag^{\oplus} \\ \quad\quad\quad\quad\quad\quad \downarrow H^{\oplus} \\ \quad\quad\quad\quad\quad\quad PhCOOH \end{array}$$

Hence solubility is : $S_2 > S_3 > S_4 > S_1$

20. (4) Solubility of salt of W_A is given by the formula (Refer section 8.23)

$$S = \left[K_{sp}\left(1 + \frac{H^{\oplus}}{K_a}\right)\right]^{1/2}$$

$$= \left[10^{-12}\left(1 + \frac{10^{-4} \times 3}{10^{-4}}\right)\right]^{1/2}$$

$$= 2 \times 10^{-6}\text{ M}$$

21. (2) S in buffer $= 2 \times 10^{-6}$ M

$$\text{S in } H_2O = \sqrt{K_{sp}} = (10^{-12})^{1/2} = 10^{-6}\text{ M}$$

$$\therefore\ \frac{S\text{ buffer}}{S\ H_2O} = \frac{2 \times 10^{-6}}{10^{-6}} = 2$$

22. (4) $H_2S \rightleftharpoons 2H^{\oplus} + S^{2-}$ $\quad \left(K_a = \frac{[H^{\oplus}]^2[S^{2-}]}{[H_2S]}\right)$

$$[S^{2-}] = \frac{K_a\,[H_2S]}{[H^{\oplus}]^2} = \frac{4 \times 10^{-21} \times 0.1}{(0.1)^2} = 4 \times 10^{-20}\text{ M}$$

For precipitation, $Q_{sp} = K_{sp}$

$$[Co^{2+}] = \frac{K_{sp}\text{ of CoS}}{[S^{2-}]} = \frac{2 \times 10^{-21}}{4 \times 10^{-20}} = 0.05\text{ M}$$

23. (3) The point D, i,e, point of inflexion represents equivalence point.

24. (1) Let x = solubility of each salt and x is small.

i. $\quad M_2X \rightleftharpoons 2M^{\oplus} + X^{2-} \quad [K_{sp} = 4x^3]$

$\qquad\qquad\qquad 2x \qquad x$

ii. $\quad QY_2 \rightleftharpoons Q^{2+} + 2Y^{\ominus} \quad [K_{sp} = 4x^2]$

$\qquad\qquad\qquad x \qquad 2x$

iii. $\quad PZ_3 \rightleftharpoons P^{3+} + 3Z^{\ominus} \quad [K_{sp} = 27x^4]$

$\qquad\qquad\qquad x \qquad 3x$

$$\therefore\ K_{sp}(M_2X) = K_{sp}(QY_2) > K_{sp}(PZ_3)$$

25. (2) **II > III > IV > I**

From the values of K_{sp} and K_f, it is evident that AgCl is more soluble than Ag I and $[Ag(CN)_2]^{\ominus}$ is more than $[Ag(NH_3)_2]^{\oplus}$. Calculation of $[Ag^{\oplus}]$ in each case revels **II > III > I > IV.**

I. $\quad Ag(CN)_2^{\ominus} \longrightarrow Ag^{\oplus} + 2\overset{\ominus}{CN}$;

$$K = \frac{1}{K_f} = \frac{[Ag^{\oplus}][CN^{\ominus}]^2}{[Ag(CN)_2^{\ominus}]} = 10^{-21}$$

Let $[Ag^{\oplus}] = x$, $[CN^{\ominus}] = 2x$,

$[Ag(CN)_2^{\ominus}] = 1.0 - x \simeq 1.0.$

$$\therefore\ K = \frac{(x)(2x)^2}{1.0} = 10^{-21} = 4x^3$$

$$\Rightarrow x = 6.3 \times 10^{-8}\text{ M}$$

II. $\quad AgCl \rightleftharpoons Ag^{\oplus} + Cl^{\ominus}$;

$K_{sp} = [Ag^{\oplus}]\,[Cl^{\ominus}] = 10^{-10}$

$\therefore\ x^2 = 10^{-10}, \Rightarrow x = 10^{-5}$ M

III.	$[Ag(NH_3)_2]^{\oplus} \longrightarrow$	$Ag^{\oplus}$	+	$2NH_3$
Initial	1.0	0		0.1
Final	$1.0 - x$	x		$2x + 0.1 \approx 0.1$ M

$$K = \frac{1}{K_f} = \frac{[Ag^{\oplus}][NH_3]^2}{[Ag(NH_3)_2^{\oplus}]} = 10^{-8}$$

Let $[Ag^{\oplus}] = x$, $[NH_3] = (2x + 0.1) \approx 0.1$

$[Ag(NH_3)_2^{\oplus}] = 1.0 - x \simeq 1.0$

$$K = \frac{x \times 0.1 \times 0.1}{1.0} = 10^{-8} \Rightarrow x = 10^{-6}\text{ M}$$

IV. $AgI \rightleftharpoons Ag^{\oplus} + I^{\ominus}$,

$x^2 = 8.3 \times 10^{-17} \Rightarrow x \Rightarrow 2.8 \times 10–9.$

II $(AgCl = 10^{-5}) >$ **III** $[(Ag(NH_3)_2^{\oplus}) = 10^{-6}] >$

I $[(Ag(CN)_2^{\ominus}) = 6.3 \times 10^{-9}] >$ **IV** $(Ag\,I = 2.8 \times 10^{-9})$

$\therefore$ II > III > I > IV

Exercises

Single Correct Answer Type

1. (1) For acidic buffer, $pH = pK_a + \log \frac{0.1}{0.1}$

$pH = pK_a = -\log(10^{-5}) = 5.$

Rule: ABA (In acidic buffer (A), on addition of S_B (B), the concentration of W_A(A) decreases and that of salt increases.

Let x M of NaOH is added.

$$pH_{new} = 5 + \log\left(\frac{0.1 + x}{0.1 - x}\right)$$

$$6 - 5 = \log\left(\frac{0.1 + x}{0.1 - x}\right)$$

$$\left(\frac{0.1 + x}{0.1 - x}\right) = \text{Antilog}(1) = 10$$

Solve for x:

$$x = 0.082 \text{ M} = \frac{0.082}{1000} \times 100$$

$$= 0.0082 \text{ mol } (100 \text{ mL})^{-1}$$

$$= 0.0082 \times 40 \text{ g } (100 \text{ mL})^{-1}$$

$$= 0.328 \text{ g}$$

2. (4) $Fe^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(OH)^{2+}(aq) + H_3O^{\oplus}(aq)$

$$\begin{array}{cccc} 1 & — & 0 & 0 \\ C(1-\alpha) & & C\alpha & C\alpha \end{array}$$

$$\left(1 - \alpha = \frac{80}{100} = 0.8, \alpha = 0.2\right)$$

$$K_a = \frac{C\alpha}{1-\alpha}$$

$$6.5 \times 10^{-3} = \frac{C \times (0.2)^2}{0.8}. \quad \therefore C = 13.0 \times 10^{-2}$$

$[H_3O^{\oplus}] = C\alpha = 13.0 \times 10^{-2} \times 0.2 = 26 \times 10^{-3}$

$pH = -\log(26 \times 10^{-3}) = -1.415 + 3 = 1.585 \approx 1.6$

3. (2) It forms basic buffer

$$pOH = pK_b + \log\left(\frac{2.5/500}{2.5/500}\right) = 4.7$$

$pH = 14 - 4.7 = 9.3$

4. (3) $\alpha = \dfrac{1}{100} = 10^{-2}$

$$BOH \rightleftharpoons B^{\oplus} + \overset{\ominus}{O}H$$

$$K_b = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 = 0.1 \times (10^{-2})^2 = 10^{-5}$$

When 0.2 mol of BCl is added, due to common ion effect of $B^{\oplus}$ ($BCl \rightleftharpoons B^{\oplus} + Cl^{\ominus}$), suppression of ionisation of BOH occurs, and α becomes α'.

$$\therefore \alpha' = \frac{K_b}{M} \text{ (M = molarity of common ion added)}$$

$$= \frac{10^{-5}}{0.2} = 5 \times 10^{-5} \text{ M}$$

5. (3)

$$BOH \rightleftharpoons B^{\oplus} + \cancel{\overset{\ominus}{O}H} \quad (K_b = 2.5 \times 10^{-6})$$

$$H^{\oplus} + \cancel{\overset{\ominus}{O}H} \rightleftharpoons H_2O \quad \left(K = \frac{1}{K_w}\right)$$

$$BOH + H^{\oplus} \rightleftharpoons B^{\oplus} + H_2O \quad K' = ?$$

$$\therefore K' = K_b \times \frac{1}{K_w} = \frac{2.5 \times 10^{-6}}{10^{-14}} = 2.5 \times 10^{8}$$

6. (3) $K_{sp}MS = [M^{2+}][S^{2-}]$

$5 \times 10^{-21} = (0.05)[S^{2-}]$

For precipitation $Q_{sp} = K_{sp}$

$$\therefore [S^{2-}] = \frac{5 \times 10^{-21}}{5 \times 10^{-2}} = 10^{-19}$$

For H_2S:

$H_2S \rightleftharpoons H^{\oplus} + HS^{\ominus}$ (K_1)

$HS^{\ominus} \rightleftharpoons H^{\oplus} + S^{2-}$ (K_2)

$$K_1 \times K_2 = \frac{[H^{\oplus}]^2 [S^{2-}]}{H_2S}$$

$$10^{-7} \times 10^{-14} = \frac{[H^{\oplus}]^2 [10^{-19}]}{0.1}$$

$[H^{\oplus}]^2 = 10^{-3}$, ⇒ [Taking negative logarithm both sides]

$-2 \log [H^{\oplus}] = 3$

$$pH = \frac{3}{2} = 1.5$$

7. (2) At half neutralisation,

$[B^{\oplus}] = [BOH]$; [Salt] = [base]

$$pOH = pK_b + \log\frac{[B^{\oplus}]}{[BOH]}$$

$pOH = pK_b$, $(pH = 8, pOH = 6)$

$\therefore pK_b = 6, K_b = 1 \times 10^{-6}$

8. (2) $HIn \rightleftharpoons H^{\oplus} + Ind^{\ominus}$;

$$pH = pK_{Ind} + \log\frac{[Ind^{\ominus}]}{[HIn]}$$

$$pH_1 = pK_{Ind} + \log\frac{20}{80} = pK_{Ind} - 2\log 2$$

$$pH_2 = pK_{Ind} + \log\frac{80}{20} = pK_{Ind} + 2\log 2$$

$\Delta(pH) = pH_2 - pH_1 = 4 \log 2 = 4 \times 0.3 = 1.2$

9. (3) Precipitation starts when $Q_{sp} = K_{sp}$.

$$K_{sp} = [Ca^{2+}][\overset{\ominus}{O}H]^2$$

$$\therefore [\overset{\ominus}{O}H] = \left(\frac{4 \times 10^{-6}}{0.01}\right)^{1/2} = 2 \times 10^{-2}$$

$pOH = -\log 2 + 2$

$pH = 14 - [-\log 2 + 2] = 12 + \log 2$

10. (3) NaZ is salt of W_A/S_B

$$\therefore pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$8.9 \times 2 = 14 + pK_a + \log 0.1$

$17.8 = 14 + pK_a - 1$

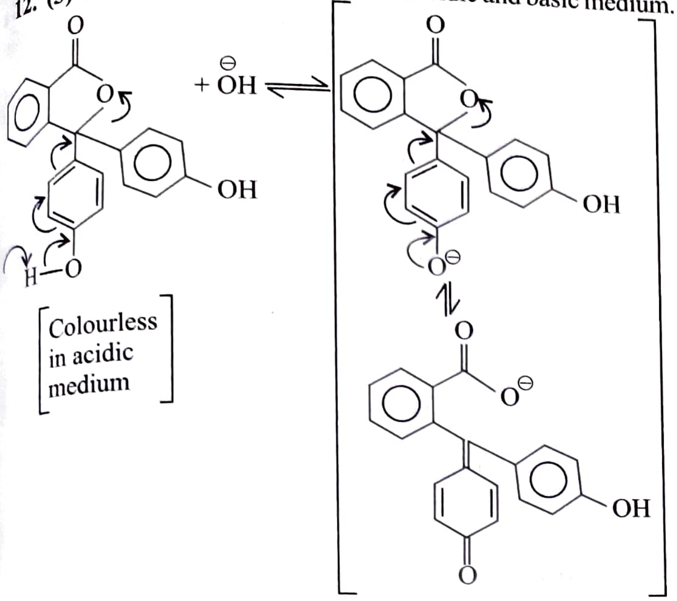
$pK_a = 4.8$,

$K_a = \text{Antilog}(-4.8) = \text{Antilog}(-4 - 0.8 + 1 - 1)$

$= \text{Antilog}(\bar{5}.2) = 1.585 \times 10^{-5} \approx 1.6 \times 10^{-5}$.

11. (1) With weak base and strong acid, phenolphthalein does not act an indicator.

12. (3) Structure of phenolphthalein in acidic and basic medium.



Quinoid structure
(Resonance stabilised)
(Pink in basic)

13. (2) Methyl orange gives red colour in acidic solution and yellow in basic solution.

14. (2) When equal volumes of $(NH_4Cl + NH_4OH)$ and metal ions are mixed (volume becomes double and concentration is halved)

$$\therefore [\overset{\ominus}{O}H] = \frac{10^6}{2},\ [M^{+n}] = \frac{0.1}{2}$$

Q_{sp} (or IP) of metal hydroxides of $M(OH)_2$ type

$$= [M^{+n}][\overset{\ominus}{O}H]^2$$

$$= \left(\frac{0.1}{2}\right)\left(\frac{10^{-6}}{2}\right)^2 = \frac{1}{8}\times 10^{-13}$$

$$= 0.125 \times 10^{-13} = 12.5 \times 10^{-11}$$

$\therefore Q_{sp} > K_{sp}$ of $Mg(OH)_2$ $(12.5 \times 10^{-11} > 3 \times 10^{-11})$.

and $Q_{sp} > K_{sp}$ of $Fe(OH)_2$ $(12.5 \times 10^{-11} > 8 \times 10^{-16})$

So both can be precipitated. Since the K_{sp} of $Fe(OH)_2$ is less than Ksp of $Mg(OH)_2$, so $Fe(OH)_2$ will be precipitated first.

Similarly, Q_{sp} (or IP) of metal hydroxides of M(OH) type

$$= [M^{+1}][\overset{\ominus}{O}H] = \left(\frac{0.1}{2}\right)\left(\frac{10^{-6}}{2}\right)$$

$$= 0.25 \times 10^{-7}$$

$\therefore Q_{sp} < K_{sp}$ of AgOH $(0.25 \times 10^{-7} < 5 \times 10^{-3})$

It can not be precipitated out. Hence $Fe(OH)_2$ will be precipitated.

15. (3) When equal volumes of $BaCl_2$ and NaF solutions are mixed. (volume becomes double and concentration is halved).

(1) $[Ba^{2+}] = \frac{10^{-3}}{2}$, $[F^{\ominus}] = \frac{2\times 10^{-2}}{2} = 10^{-2}$

Q_{sp} of $BaF_2 = [Ba^{2+}][F^{\ominus}]^2$

$= (0.5 \times 10^{-3})(10^{-2})^2 = 5 \times 10^{-6}$

$Q_{sp} > K_{sp}$ $(5 \times 10^{-6} > 1.7 \times 10^{-7})$ will be precipitated.

(2) $[Ba^{2+}] = \frac{10^{-3}}{2}$, $[F^{\ominus}] = \frac{1.5\times 10^{-2}}{2}$

Q_{sp} of $BaF_2 = [Ba^{2+}][F^{\ominus}]^2 = (0.5 \times 10^{-2})(0.75 \times 10^{-2})^2$

$= 0.28 \times 10^{-6}$

$Q_{sp} > K_{sp}$. Hence precipitation occurs.

(3) $[Ba^{2+}] = \frac{1.5\times 10^{-3}}{2}$, $[F^{\ominus}] = \frac{10^{-2}}{2}$,

$$Q_{sp} \text{ of } BaF_2 = [Ba^{2+}][F^{\ominus}]^2 = \left(\frac{1.5\times 10^{-3}}{2}\right)\left(\frac{10^{-2}}{2}\right)^2$$

$$= 0.187 \times 10^{-7}$$

$Q_{sp} < K_{sp}$ $(0.187 \times 10^{-7} < 1.7 \times 10^{-7})$

So solution in (c) will not precipitate out.

(4) $[Ba^{2+}] = \frac{2\times 10^{-2}}{2} = 10^{-2}$ M,

$[F^{\ominus}] = \frac{2\times 10^{-2}}{2} = 10^{-2}$ M

Q_{sp} $BaF_2 = (10^{-2})(10^{-2})^2 = 10^{-6}$

$\therefore Q_{sp} > K_{sp}$. Hence precipitation occurs.

16. (4) i. $Ag_2CrO_4 \rightleftharpoons \underset{2S}{2Ag^{\oplus}} + \underset{S}{CrO_4^{2-}}$ (in H_2O)

$4S^3 = K_{sp}$;

$$S_{H_2O} = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{9\times 10^{-12}}{4}\right)^{1/3}$$

$$= (2.25)^{1/3} \times 10^{-4}\ M$$

ii. On adding 0.1 M $AgNO_3$

$(AgNO_3 \longrightarrow \underset{0.1\ M}{Ag^{\oplus}} + \underset{0.1\ M}{NO_3})$

Due to common ion $(Ag^{\oplus})$, the solubility of Ag_2CrO_4 is suppressed.

Total $[Ag^{\oplus}] = (2S + 0.1) \approx 0.1$

Let the solubility is S_1.

$$\therefore S_1 = \frac{K_{sp}}{[Ag^{\oplus}]^2_{\text{externally added}}}$$

$$= \frac{9\times 10^{-12}}{0.1\times 0.1} = 9\times 10^{-10}\ M$$

iii. On adding 0.1 M Na_2CrO_4

$(Na_2CrO_4 \longrightarrow \underset{2\times 0.1\ M}{2Na^{\oplus}} + \underset{0.1\ M}{CrO_4^{2-}})$

Again due to common ion (CrO_4^{2-}), the solubility of Ag_2CrO_4 is suppressed.

Let the solubility is S_2.

Tota $[CrO_4^{2-}] = (S + 0.1) \approx 0.1$

$$\text{Ag}_2\text{CrO}_4 \rightleftharpoons \underset{2S_2}{2\text{Ag}^{\oplus}} + \underset{(S_2+0.1)\,\approx\, 0.1}{\text{CrO}_4^{2-}}$$

$$K_{sp} = [2S_2]^2[0.1]$$

$$\therefore S_2 = \left(\frac{K_{sp}}{4\times 0.1}\right)^{1/2} = \left(\frac{9\times 10^{-12}}{4\times 0.1}\right)^{1/2}$$

$$= 22.5 \times 10^{-6} = 2.25 \times 10^{-7}$$

Hence, the solubility order is II < III < I.

Note: In such problems, instead of solving the exact value, try to get the approximate data to check the comparative solubilities).

17. (1) (Assume $[\text{Al}^{3+}] = [\text{Zn}^{2+}]$)

The compound which have less K_{sp} value will be precipitated first. Since the K_{sp} of Al(OH)_3 is less than K_{sp} of Zn(OH)_2. So former is precipitated.

Note: In such questions no need to calculating the exact value only approximation is required.

$$[\overset{\ominus}{\text{O}}\text{H}]_{\min} \text{ for Al}^{3+} = \left(\frac{K_{sp} \text{ of Al(OH)}_3}{[\text{Al}^{3+}]}\right)^{1/3}$$

$$[\overset{\ominus}{\text{O}}\text{H}]_{\min} \text{ for Zn}^{2+} = \left(\frac{K_{sp} \text{ of Zn(OH)}_2}{[\text{Zn}^{2+}]}\right)^{1/2}$$

18. (1) $\text{PbSO}_4\text{(s)} \rightleftharpoons \text{Pb}^{+2}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \quad (K_{sp}) \quad \ldots\text{(i)}$

$\text{HSO}_4^{\ominus}\text{(s)} \rightleftharpoons \text{H}^{\oplus}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \quad (K_a) \quad \ldots\text{(ii)}$

Subtracting equation (ii) from (i), then

$\text{PbSO}_4 + \text{H}^{\oplus}\text{(aq)} \rightleftharpoons \text{Pb}^{2+}\text{(aq)} + \text{HSO}_4^{\ominus}\text{(aq)} \quad (K_{eq})$

$$\therefore K_{eq} = \frac{K_{sp}}{K_a} = \frac{1.8\times 10^{-8}}{1.0\times 10^{-2}} = 1.8\times 10^{-6}$$

19. (2) Factual statement.

20. (2) $\text{Mg(OH)}_2 \longrightarrow \underset{\text{S}}{\text{Mg}^{2+}} + \underset{2\text{S}}{2\overset{\ominus}{\text{O}}\text{H}}$

Let S_1 is the solubility in 0.01 M MgCl_2 (common ion Mg^{2+})

$\therefore [\text{Mg}^{2+}] = (\text{S}_1 + 0.01) \approx 0.01$

$[\overset{\ominus}{\text{O}}\text{H}] = 2\text{S}_1$

$K_{sp} = (0.01)(2\text{S}_1)^2$

$$S_1 = \left(\frac{K_{sp}}{4\times 0.01}\right)^{1/2} = \left(\frac{10^{-12}}{4\times 10^{-2}}\right)^{1/2} = 0.5 \times 10^{-5}\text{ M}$$

$\therefore [\overset{\ominus}{\text{O}}\text{H}] = 2S_1 = 2 \times 0.5 \times 10^{-5} = 10^{-5}$ M

pOH = 5, pH = 14 – 5 = 9

21. (1) Since all compounds (MA, MB, MC, and MD) are univalent type. All will have the same formula of solubility in H_2O (i.e., $\sqrt{K_{sp}}$). Same concentration of common ion ($\text{M}^{\oplus}$) is added, so solubilities of all will be suppressed.

Hence, the compound with least K_{sp} value will be precipitated, i.e., MA with $K_{sp} = 1.8 \times 10^{-10}$.

22. (3) The two K_{sp} values do not differ very much. So it is a case of simultaneous equilibria, where the concentration of any species can not be neglected.

$$\frac{\cancel{[\text{Sr}^{2+}]}[\text{F}^{\ominus}]^2}{\cancel{[\text{Sr}^{2+}]}[\text{CO}_3^{2-}]} = \frac{K_{sp}\ \text{SrF}_2}{K_{sp}\ \text{SrCO}_3} = \frac{7.9\times 10^{-10}}{7.0\times 10^{-10}} = 1.128$$

$\therefore [\text{F}^{\ominus}]^2 = 1.28 \times [\text{CO}_3^{2-}] = 1.128 \times 1.2 \times 10^{-3}$

$= 13.5 \times 10^{-4}$

$\therefore [\text{F}^{\ominus}] = (13.5 \times 10^{-4})^{1/2}$

$= 3.674 \times 10^{-2} \approx 3.7 \times 10^{-2}$ M.

23. (1) $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^{\oplus} + \text{S}^{2-}$

$$\therefore K_a = \frac{[\text{H}^{\oplus}]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-21} = \frac{0.1\times 0.1\times[\text{S}^{2-}]}{0.1}$$

$\therefore [\text{S}^{2-}] = 10^{-20}\text{ M} = 10^{-20} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{3}$ ions

24. (2) Factual statement.

25. (2) M_2X: Solubility of $\text{M}_2\text{X} = \sqrt[3]{\dfrac{K_{sp(\text{M}_2\text{X})}}{4}}$

MX: Solubility of $\text{MX} = \sqrt{K_{sp(\text{MX})}}$

MX_3: Solubility of $\text{MX}_3 = \sqrt[4]{\dfrac{K_{sp(\text{MX}_3)}}{27}}$

Clearly, solubility is maximum for MX_3 and then M_2X.

26. (3) $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

$\Rightarrow$ At equivalence point, a salt of weak acid, strong base is formed.

$$\Rightarrow \text{pH} = 7 + \frac{1}{2}(\text{p}K_a + \log C)$$

Here C = concentration of salt $= \dfrac{0.2\times 500}{500+500} = 0.1$ M

[Check that 500 mL of CH_3COOH is also required]

$$\Rightarrow \text{pH} = 7 + \frac{1}{2}(4.74 + \log 0.1) = 8.87$$

27. (2) NaX: Salt of weak acid, strong base.

$$\Rightarrow \alpha = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}} = \sqrt{\frac{10^{-14}}{10^{-5}\times 0.1}} = 10^{-4}$$

$\Rightarrow$ % hydrolysis = 0.01%

(Check that approximation is valid)

28. (1) K_b for $\text{X}^{\ominus} = 10^{-10}$

$$\Rightarrow K_a \text{ for HX} = \frac{K_w}{K_b(\text{X}^{\ominus})} = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

$$\Rightarrow \text{pH} = \text{p}K_a + \log\frac{[\text{X}^{\ominus}]}{[\text{HX}]} = \text{p}K_a = 4$$

29. (3) HA: $K_a = 10^{-4}$

$HA + NaOH \rightleftharpoons NaA + H_2O$

Clearly, the reverse reaction is the hydrolysis reaction.

$$\Rightarrow K_{\text{Required}} = \frac{1}{K_h} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

30. (1) $2NH_3 \rightleftharpoons NH_4^{\oplus} + NH_2^{\ominus}$

$[NH_4^{\oplus}] = [NH_2^{\ominus}] = \sqrt{K_{NH_3}} = 10^{-15}$ M

1 dm^3 of solution contains 10^{-15} moles = $6.02 \times 10^{23} \times 10^{-15}$ molecules of $NH_2^{\ominus}$.

1 mm^3 of solution contains $6.02 \times 10^{23} \times 10^{-15} \times 10^{-6}$ = 602 $NH_2^{\ominus}$ ions.

31. (1) Use: $[H^{\oplus}]_{\text{mix}} = \sqrt{\Sigma K_{ai} C_i}$

$$= \sqrt{1.8 \times 10^{-4} \times 0.1 + 3.1 \times 10^{-4} \times 0.1}$$

$$= \sqrt{4.9 \times 10^{-5}} \text{ M} = 7 \times 10^{-3} \text{ M}$$

32. (4)

	NH_4 +	NaOH	$\longrightarrow$ NH_4OH + NaCl
mmol	50×0.2 = 10	75×0.1 = 7.5	
mmol	10 – 7.5 = 2.5	—	7.5

$\Rightarrow$ This will result in a basic buffer.

$$\Rightarrow pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= 4.74 + \log \frac{2.5}{7.5} = 4.27$$

$\Rightarrow pH = 14 - 4.27 = 9.73$

33. (3) Find the $[Ag^{\oplus}]$ in all the saturated solutions.

$$[Ag^{\oplus}]_{\text{in AgCl}} = \sqrt{K_{sp}\ AgCl} = \sqrt{1.8 \times 10^{-10}} \text{ M;}$$
$$= 0.134 \times 10^{-4} \text{ M}$$

$$[Ag^{\oplus}]_{\text{in AgBr}} = \sqrt{K_{sp}\ AgBr} = \sqrt{5.0 \times 10^{-13}} \text{ M}$$
$$= (0.5 \times 10^{-12})^{1/2} \text{ M}$$
$$= 0.007 \times 10^{-4} \text{ M}$$

$$[Ag^{\oplus}]_{\text{in } Ag_2CrO_4} = \sqrt[3]{\frac{K_{sp}\ Ag_2CrO_4}{4}}$$
$$= \sqrt[3]{\frac{2.4 \times 10^{-12}}{4}} \text{ M}$$
$$= (0.6 \times 10^{-12})^{1/2} \text{ M}$$
$$= 0.84 \times 10^{-4} \text{ M}$$

$\Rightarrow [Ag^{\oplus}]$ is maximum in saturated solution of Ag_2CrO_4.

34. (3) $\underset{\text{Red}}{HIn} \xrightleftharpoons{K_{Ind}} H^{\oplus} + \underset{\text{Blue}}{Ind^{\ominus}}$

Use: $pH = pK_{Ind} + \log \frac{[Ind^{\ominus}]}{[HIn]}$;

$pK_{Ind} = -\log (3 \times 10^{-5}) = 4.52$

75% Red $\Rightarrow \frac{[HIn]}{[Ind^{\ominus}]} = \frac{3}{1}$

$\Rightarrow pH = pK_{Ind} + \log \frac{1}{3} = 4.05$

75% Blue $\Rightarrow \frac{[HIn]}{[Ind^{\ominus}]} = \frac{1}{3}$

$\Rightarrow pH = pK_{Ind} + \log \frac{3}{1} = 5.00$

35. (1) NaCl is salt of S_A/S_B. So it is neutral and pH = 7.

36. (2) $CH_3COOH \longrightarrow CH_3COO^{\ominus} + H^{\oplus}$

Only the HCl provides common ion $H^{\oplus}$ and so it will suppress the ionisation of acetic acid.

37. (2) $H_3O^{\oplus} = 10^{-9}$ M.

Since the concentration of $H_3O^{\oplus}$ is $<10^{-6}$ M. So concentration of $H_3O^{\oplus}$ is calculated from ionisation of water and its common effect, so the value will lie between 6 and 7.

38. (3) $\underset{\text{Base}}{NH_3} + H_2O \longrightarrow \underset{C_A}{NH_4^{\oplus}} + \overset{\ominus}{OH}$

$\underset{\text{Acid}}{NH_3} \longrightarrow \underset{C_B}{NH_2^{\ominus}} + H^{\oplus}$

So $NH_4^{\oplus}$ and $NH_2^{\ominus}$ are conjugate pair of NH_3.

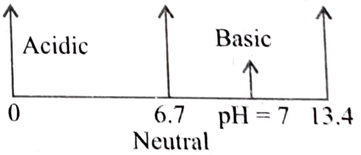
39. (1) Bronsted acid is which gives $H^{\oplus}$ ions and Bronsted base is which accepts $H^{\oplus}$ ion.

So H_2S gives $H^{\oplus}$ ions but cannot accept $H^{\oplus}$. While others H_2O, $HCO_3^{\ominus}$, NH_3 can give and accept $H^{\oplus}$ ions.

40. (2) Due to common ion ($NH_4^{\oplus}$), from NH_4Cl, it suppresses the ionisation of NH_4OH, so as to give less concentration, of $\overset{\ominus}{OH}$ ions, so that only the hydroxides of III group can precipitate, not the hydroxides of higher group, since K_{sp} of the hydroxides of III group is lower than the K_{sp} of the hydroxides of higher group.

41. (2) $pK_w = 13.4$.

If we calculate the pH of H_2O from the above value, it come to be 6.7. (Since cone, of $H^{\oplus}$ and $\overset{\ominus}{OH}$ is equal). So new scale is made from 0 to 13.4



So, at pH = 7, Solution is basic.

42. (3) Buffer capacity

$$= \frac{\text{Number of mols / litre of acid or base added}}{\text{change in pH or pOH}}$$

$$= \frac{2}{3.4 - 2.9} = \frac{2}{0.5} = 4$$

43. (3) i. $AgCl + H_2O \longrightarrow Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$ ...S_1

ii. AgCl in 0.01 M $CaCl_2$, ...S_2

Concentration of $Cl^{\ominus} = 2 \times 0.01 = 0.02$ M

iii. AgCl in 0.01 M NaCl, ...S_3

Concentration of $Cl^{\ominus} = 0.01$ M

iv. AgCl is 0.05 M. $AgNO_3$, ...S_4

Concentration of $Ag^{\oplus} = 0.05$.

Since both $Cl^{\ominus}$ ions and $Ag^{\oplus}$ ions acts as common ion. So larger the concentration of $Ag^{\oplus}$ or $Cl^{\ominus}$ ions, more is the suppression of ionisation of AgCl and hence less will be solubility of AgCl.

∴ Solubility order

$S_1 > S_3 > S_2 > S_4$

44. (1) Salt of S_A/S_B do not undergo hydrolysis. So Na_2SO_4 is a salt of S_A/S_B.

45. (1) Salt of S_A/S_B do not hydrolyse in H_2O. So pH does not change on adding KCl to H_2O.

46. (4) Salt of W_A/S_B hydrolyse and the solution is basic, i.e., $pH > 7$.

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

47. (3) Initial pH or pOH = 7, ∴ $[\overset{\ominus}{OH}] = 10^{-7}$ M.

Final pH = 12, ∴ pOH = 2, $[\overset{\ominus}{OH}] = 10^{-2}$ M.

Increase in $[\overset{\ominus}{OH}] = \dfrac{10^{-2}}{10^{-7}} = 10^{5}$ times

48. (4) $0.05\ M_{H_2SO_4} = 2 \times 0.05\ N_{H_2SO_4} = 0.1$ N

$\therefore [H_3O^{\oplus}] = [0.1] = 10^{-1}$

$-\log [H_3O^{\oplus}] = -\log [10^{-1}] = 1$

$pH = 1$

49. (1) pOH = 13, pH = 14 – 13 = 1

Hence, solution is highly acidic.

50. (3) $NH_3 + H_2O \longrightarrow NH_4^{\oplus} + \overset{\ominus}{OH}$

$H_2O + H_2O \longrightarrow H_3O^{\oplus} + \overset{\ominus}{OH}$

Due to common ion $[OH^{\ominus}]$, the self ionisation of H_2O is suppressed so the concentration of $H_3O^{\oplus}$ is decreased.

51. (2) $CH_3COOH \longrightarrow CH_3COO^{\ominus} + H^{\oplus}$

$CH_3COONa \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$

Due to common ion $(CH_3COO^{\ominus})$, the suppression of ionisation of CH_3COOH takes place, so the concentration of $H^{\oplus}$ decreases, so pH increases. So pH must be more than 4.3.

52. (3) Bronsted acid and base is that which can donate and accept $H^{\oplus}$ ions. So $HSO_4^{\ominus}$ can accept and donate $H^{\oplus}$ ions.

53. (3) Lewis acid is that which is e^- deficient and can accept lone pair of e^- s. So BF_3 can accept a lone pair of e^- s.

54. (4) Lewis base is that which can donate a lone pair of e^- s. All except $AlCl_3$ have lone pair of e^- s and can donate. So $AlCl_3$ is not a lewis base.

55. (4) Conjugate base $\overset{\ominus}{OH}$ is O^{2-},

$\overset{\ominus}{OH} \longrightarrow O^{2-} + H^{\oplus}$

56. (3) Largest pH, will be of the most basic solution, so $\dfrac{M}{10}$ NaOH, will have largest pH.

57. (4) i. K_2SO_4 is salt of S_A/S_B and do not hydrolyse so pH = 7

ii. pH of pure $H_2O = 7$

iii. pH of 10^{-2} mols of HCl per litre = 2

iv. pH of weak bae NH_4OH will be more than 7.

58. (4) mEq of NaOH $= 20 \times \dfrac{1}{20} = 1$

mEq of HCl $= 10 \times \dfrac{1}{10} = 1$

So, salt of S_A/S_B (NaCl) will be formed which do not hydrolyse and pH = 7. So at pH = 7, litmus has no effect. Since, blue litmus turns red a acidic solution, and red litmus turns blue, a basic solution.

i. phenolphthalein solution turns pink a basic solution of pH > 7.

ii. Methyl orange turns red a acidic solution of pH < 7.

59. (1) On heating H_2O at 350 K, the self ionisation of H_2O, increases

$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + \overset{\ominus}{OH}$

So the concentration of $[H_3O^{\oplus}]$ and $[\overset{\ominus}{OH}]$ both increases, so the pH increases or pOH decreases.

60. (4) $A_2B_3 \rightleftharpoons \underset{2S}{2A^{3+}} + \underset{3S}{3B^{2-}}$

$K_{sp} = (2S)^2 (3S)^3 = 108S^5 = 108 \times (10^{-4})^5$

$= 108 \times 10^{-20} = 1.08 \times 10^{-20} = 1.08 \times 10^{-18}$

61. (2) $HgCl_2 \rightleftharpoons \underset{2S}{Hg^{2+}} + \underset{2S}{2Cl^{\ominus}}$

$K_{sp} = 4S^3.$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4 \times 10^{-15}}{4}} = 10^{-5}$$

$\therefore 2S = 2 \times 10^{-5} = [Cl^{\ominus}]$

62. (3) $K_w = [H_3O^{\oplus}][\overset{\ominus}{OH}]$

$= 10^{-6.7} \times 10^{-6.7} = 10^{-13.4}$

63. (1) $PbSO_4 \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{S}{SO_4^{2-}}$

	$Na_2SO_4 \longrightarrow$	$2Na^{\oplus}$	$+\ SO_4^{2-}$
Intial	0.01	0	0
Final	0	2×0.01	0.01

(Since Na_2SO_4 is salt of S_A/S_B it is completely ionised).

$\therefore SO_4^{2-} = (x + 0.01) = 0.01$ (Since x is very small)

$\therefore K_{sp}$ of $PbSO_4 = [Pb^{2+}][SO_4^{2-}]$

$1.25 \times 10^{-9} = x \times 0.01$

$$\therefore x = \frac{1.25 \times 10^{-9}}{0.01} = 1.25 \times 10^{-7}\ \text{mol L}^{-1}$$

64. (3) $pH = 10, pOH = 4, [\overset{\ominus}{O}H] = 10^{-4}$ M

$Ba(OH)_2 \longrightarrow Ba^{2+} + 2\,\overset{\ominus}{O}H$

$[\overset{\ominus}{O}H] = 10^{-4}$.

(Since total concentration of $\overset{\ominus}{O}H = 10^{-4}$).

$\therefore K_{sp} = [Ba^{2+}][\overset{\ominus}{O}H]^2$

$10^{-9} = x \times (10^{-4})^2$

$\therefore x = 10^{-1} = [Ba^{2+}]$

65. (2) $pH = 12, pOH = 2, [\overset{\ominus}{O}H] = 10^{-2}$ M

$[\overset{\ominus}{O}H] = 10^{-2}\text{ M} = 10^{-2} \times 40\text{ g L}^{-1} = 0.4\text{ g L}^{-1}$

66. (2) (1) 10^{-10} M HCl, since $[H_3O^{\oplus}] < 10^{-6}$ M, so pH is less than 7, because of the acidic solution.

(2) 10^{-4} M NaOH, since $[\overset{\ominus}{O}H] = 10^{-4}$ M, pOH = 4, pH = 10.

(3) 10^{-10} M NaOH, Since $[\overset{\ominus}{O}H] < 10^{-6}$ M, pH is slightly more than 7, because of the basic solution.

67. (1)

	HA	+ $H_2O \rightleftharpoons$	$H_3O^{\oplus}$	+ $A^{\ominus}$
Inital	1	0	0	0
Final	$C(1-\alpha)$		$C\alpha$	$C\alpha$

$[H_3O^{\oplus}] = C\alpha \left(\alpha = \frac{40}{100} = 0.4\right)$

$= 0.2 \times 0.4 \qquad (C = 0.2\text{ M})$

$= 0.08.$

68. (1) $N_1V_1(HCl) = N_2V_2(NaOH)$

$x \times 20 = 40 \times 0.05$

$x = 0.1$

$\therefore$ M of HCl = 0.1

$[H_3O^{\oplus}] = 0.1 = 10^{-1}$

pH = 1

69. (1)

	HA	+ $H_2O \rightleftharpoons$	$H_3O^{\oplus}$	+ $A^{\ominus}$
Initial	1	0	0	0
Final	$C(1-\alpha)$		$C\alpha$	$C\alpha$

$[H_3O^{\oplus}] = C\alpha = 0.1 \times 0.01 = 10^{-3}$

pH = 3, pOH = 11

70. (1) pH = 5.0, pOH = 11

$pH_1 = 5.0, [H_3O^{\oplus}] = 10^{-5}$ M

New $pH_2 = 2.0, [H_3O^{\oplus}] = 10^{-2}$ M

Increase in concentration of $[H_3O^{\oplus}]$

$$= \frac{10^{-2}}{10^{-5}} = 10^3 = 1000 \text{ times}$$

71. (3) $AgCl \rightleftharpoons Ag^{\oplus} + Cl^{\ominus}$

$x \qquad x$

	NaCl	$\longrightarrow$	$Na^{\oplus}$	+ $Cl^{\ominus}$
Inital	0.1		0	0
Final	0		0.1	0.1

(NaCl is a salt of S_A/S_B, which is completely ionised).

$\therefore Cl^{\ominus} = (x + 0.1) \approx 0.1$ (Since x is very small)

$\therefore K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$

$1.2 \times 10^{-10} = x \times 0.1$

$$x = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9}\text{ M}$$

72. (2) Higher the K_{sp}, more soluble is that compound in H_2O.

$\therefore K_{sp}$ of FeS (11×10^{-20}) is highest.

So it is more soluble and has maximum solubility in H_2O.

73. (4) $M_2SO_4 \rightleftharpoons 2M^{\oplus} + SO_4^{2-}$

$2S \qquad S$

$K_{sp} = (2S)^2(S) = 4S^3$.

$$\therefore S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.2 \times 10^{-5}}{4}} = 2 \times 10^{-2}\text{ M}$$

74. (1) $[Pb(IO_3)_2] \rightleftharpoons Pb^{2+} + 2IO_3^{\ominus}$

$2S \qquad S$

$K_{sp} = 4S^3$.

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.2 \times 10^{-14}}{4}} = 2 \times 10^{-5}\text{ M}$$

75. (3) $K_b = 10^{-5}, \; pK_b = 5$

NH_4OH is a week base

$\therefore [\overset{\ominus}{O}H] = C\alpha$

$[\overset{\ominus}{O}H] = \sqrt{K_b \times C}$

$$pOH = \frac{1}{2}(pK_b - \log C)$$

$$= \frac{1}{2}(5 - \log 0.1) = \frac{1}{2}(5 + 1) = 3$$

pH = 14 – pOH = 14 – 3 = 11

76. (4) Indicator used for the titration of *WA* and *SB* is phenolphthaleim. Since the pH range near the end point is 8 to 10.

77. (2) $AgCl \rightleftharpoons Ag^{\oplus} + Cl^{\ominus}$

$KCl \longrightarrow K^{\oplus} + Cl^{\ominus}$

Due to common ion effect of $Cl^{\ominus}$, the suppression of ionisation of AgCl, takes place and solubility of AgCl decreases.

78. (2) Buffer (A):

$$pH_1 = pK_a + \log\left(\frac{x}{y}\right) \qquad \text{...(i)}$$

Buffer (B):

$$pH_2 = pK_a + \log\left(\frac{x}{y}\right) \qquad \text{...(ii)}$$

Since $x > y$.

$$\therefore pH_1 - pH_2 = 1 = \log\frac{x}{y} - \log\frac{y}{x}$$

$$\therefore 1 = 2\log\frac{x}{y}$$

$$\log \frac{x}{y} = \frac{1}{2} = 0.5$$

$$\frac{x}{y} = \text{Antilog } (0.5) = 3.17$$

79. (2) Since K_{sp} of $CaCO_3$ and $BaCO_3$ are very close. So concentration of any species cannot be neglected.

Let the solubility of $CaCO_3$ and $BaCO_3$ are x and y M.

$$\therefore\ CaCO_3 \rightleftharpoons \underset{x}{Ca^{2+}} + \underset{x}{CO_3^{2-}}$$

$$BaCO_3 \rightleftharpoons \underset{y}{Ba^{2+}} + \underset{y}{CO_3^{2-}}$$

Total $[CO_3^{2-}] = (x + y)$

$\therefore K_{sp}$ of $CaCO_3 = [Ca^{2+}][CO_3^{2+}] = x(x + y)$

K_{sp} of $BaCO_3 = [Ba^{2+}][CO_3^{2-}] = y(x + y)$

$\therefore x(x + y) = 10^{-8}$ ...(i)

$y(x + y) = 5 \times 10^{-9}$ ...(ii)

$$\frac{5 \times 10^{-9}}{10^{-8}} = \frac{y(x + y)}{x(x + y)}$$

$$\therefore \frac{y}{x} = 5 \times 10^{-1}$$

$y = 0.5x$

Substitute the value of y in (i) or (ii).

$x(x + 0.5x) = 10^{-8}$

$x = 0.8 \times 10^{-4}$

$y = 0.5 \times 0.8 \times 10^{-4}$

$\therefore [Ca^{2+}] = x = 0.8 \times 10^{-4}$

$\therefore [Ba^{2+}] = y = 0.4 \times 10^{-4}$

$[CO_3^{2-}] = (x + y) = 1.2 \times 10^{-4}$

80. (4) $pH_1 = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$

$$pH_1 = pK_a + \log\left(\frac{x_1}{y_1}\right)$$

$$pH_2 = pK_a + \log\left(\frac{x_2}{y_2}\right)$$

$$pH_2 - pH_1 = \log \frac{x_2}{y_2} - \log \frac{x_1}{y_1}$$

$$2 = \log\left(\frac{x_2/y_2}{x_1/y_1}\right)$$

$$\therefore \frac{x_2/y_2}{x_1/y_1} = 10^2 = 100$$

This is only possible, if the concentration of salt is increased by 10 times and the concentration of acid is decreased by 10 times.

81. (2) Buffer solution is a mixture of

W_A + salt of W_A/S_B

or a mixture of W_B + Salt of W_B/S_A.

So ($NaH_2PO_4 + Na_2HPO_4$) is a buffer.

1. $[HCl + NaCl,]$	S_A + Salt of S_A/S_B (not buffer)
2. $[NaH_2PO_4 + Na_2HPO_4]$	W_A + Salt of W_A/S_B (it is a buffer)
3. $[CH_3COOH + NaCl]$	W_A + Salt of S_A/S_B (not buffer)
4. $[NH_4OH + NH_3]$	$W_B + W_B$ (not buffer)

82. (4) mEq of $CH_3COOH = 20 \times \frac{1}{10} = 2$

mEq of $NaOH = 16 \times \frac{1}{10} = 1.6$

So 1.6 mEq of NaOH reacts with 1.6 mEq of CH_3COOH to form 1.6 mEq of salt CH_3COONa and ($2 - 1.6 = 0.4$ mEq) of $W_A(CH_3COOH)$ is left and an acidic buffer is formed. So to calculate pH, buffer equation is used.

$$pH = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right) = 4.74 + \log\left(\frac{1.6}{0.4}\right)$$

$$= 4.74 + 2 \log 2$$

$$= 4.74 + 2 \times 0.3010 = 5.35$$

83. (1) Since K_{sp} of $CaCO_3$ and CaC_2O_4 are very close, so concentration of any species cannot be neglected.

Let the solubilities of $CaCO_3$ and CaC_2CO_4 are x and y M.

$$\underset{x}{CaCO_3} \rightleftharpoons \underset{x}{Ca^{2+}} + CO_3^{2-}$$

$$CaC_2O_4 \rightleftharpoons \underset{y}{Ca^{2+}} + \underset{y}{CO_3^{2-}}$$

Total $[Ca^{2+}] = x + y$

K_{sp} of $CaCO_3 = [Ca^{2+}][CO_3^{2-}] = (x + y)x$

K_{sp} of $CaC_2O_4 = [Ca^{2+}][C_2O_4^{2-}] = (x + y)y$

$\therefore x(x + y) = 4.7 \times 10^{-9}$ ...(i)

$y(x + y) = 1.3 \times 10^{-9}$ ...(ii)

$$\frac{x}{y} = \frac{4.7 \times 10^{-9}}{1.3 \times 10^{-9}}$$

$\therefore x = 3.615y$

Substituting the value of x in equation (i) or (ii)

$3.615y(3.615y + y) = 4.7 \times 10^{-9}$

$3.615 \times 4.615y^2 = 4.7 \times 10^{-9}$

$$\therefore y = \left(\frac{4.7 \times 10^{-9}}{16.68}\right)^{1/2} = 1.67 \times 10^{-5}\ \text{M}$$

$x = 6.03 \times 10^{-5}$ M

$[Ca^{2+}] = x + y = (6.03 \times 10^{-5} + 1.67 \times 10^{-5})$

$= 7.707 \times 10^{-5}$ M

84. (4) $Ca_3(PO_4)_2 \rightleftharpoons \underset{3x}{3Ca^{2+}} + \underset{2x}{2PO_4^{3-}}$

$K_{sp} = (3x)^3(2x)^2 = 108x^5$

$\therefore$ Units of K_{sp} is $(\text{concentration})^5 =$
$(\text{mol dm}^{-3})^5 = \text{mol}^5\ \text{dm}^{-15} = \text{mol}^5\ \text{dm}^{-15}$

85. (4) $M_1V_1 = M_2V_2$

$10^{-5} \times 1 = M_2 \times 1000$

$M_2 = 10^{-8}$

$[H_3O^{\oplus}] = 10^{-8}$ M

Since the $[H_3O^{\oplus}] < 10^{-6}$

So pH ≈ 6.98

86. (3)

1. It is a mixture of S_A + salt of S_A/S_B. So pH is due to S_A and is less than 7.
2. mEq of $H_2SO_4 = 100 \times 0.2 \times 2 = 40$

   mEq of $NaOH = 100 \times 0.3 = 30$

   So 30 mEq of NaOH will react with 30 mEq of H_2SO_4, So 10 mEq of H_2SO_4 (strong acid will be left)

   So pH will be less than 7.
3. mEq of $CH_3COOH = 100 \times 0.1 = 10$

   mEq of $KOH = 100 \times 0.1 = 10$

   So 10 mEq of W_A (CH_3COOH) will react with 10 mEq of KOH (S_B) to give 10 mEq of salt (CH_3COONa). It is a salt of W_A/W_B.

   So its pH will be greater than 7.

   $$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$
4. mEq of $HNO_3 = 25 \times 0.1 = 2.5$

   mEq of $NH_3 = 25 \times 0.1 = 2.5$

   So 2.5 mEq of HNO_3 will react with 2.5 mEq of NH_3 to give 2.5 mEq of NH_4NO_3, which is a salt of W_B/S_A, and its pH is always less than 7.

   $$pH = \frac{1}{2}(pK_w - pK_b - \log C)$$

87. (1) $CaF_2 \rightleftharpoons Ca^{2+} + 2F^{\ominus}$

$\qquad\qquad x \qquad 2x$

Total concentration of $[F^{\ominus}] = 4 \times 10^{-4}$ M

$\therefore 2x = 4 \times 10^{-4}$

$x = 2 \times 10^{-4}$

$\therefore K_{sp} = 4x^3 = 4 \times (2 \times 10^{-4})^3 = 3.2 \times 10^{-11}$

88. (2) An acid base indicator changes its colour when $pH = pK_a$ or $pOH = pK_b$.

$\therefore K_b = 10^{-10}, pK_b = 10$

$\therefore pOH = 10, pH = 14 - 10 = 4$

pH = 4

89. (2) NH_4OH is W_B

$$\therefore [\overset{\ominus}{O}H] = C\alpha = \sqrt{K_b \times c} = \sqrt{1.8 \times 10^{-5} \times 0.1}$$
$$= 1.34 \times 10^{-3} \text{ M}$$

90. (1) pH stands for French word puissance de hydrogen which means power of hydrogen ions.

91. (4) pH = 2, $\therefore [H_3O^{\oplus}] = 10^{-2}$ M

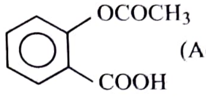
pH = 6, $\therefore [H_3O^{\oplus}] = 10^{-6}$ M

$$\therefore \frac{10^{-2}}{10^{-6}} = 10^4$$

92. (1) W_A (CH_3COOH) is titrated with S_B(NaOH) and 20% of the W_A is neutralised, so 20% of the salt of W_A/S_B (CH_3COONa) is formed and 80% of the W_A (CH_3COOH) is left. So an acidic buffer if formed.

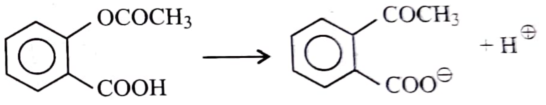
$\therefore$ [Acid] = 80; [Salt] = 20

$$pH = pK_a + \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$$
$$= 4.7447 + \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$$
$$= 4.7447 + \log\frac{1}{4}$$
$$= 4.7447 - 2\log 2 = 4.7447 - 2 \times 0.3010 = 4.14$$

93. (4) 

(Acetyl salicylic acid) (Aspirin)

Aspirin is a weak acid and its ionisation is suppressed due to common ion effect in acidic medium, i.e., in stomach. Therefore, aspirin is unionised in stomach whereas in small intestine its pH is basic. So the ionisation of aspirin increases, that is why it is completely ionised in small intestine.



Base in intenstine (NaOH) ⟶ $Na^{\oplus} + \overset{\ominus}{O}H$

$H^{\oplus}$ and $\overset{\ominus}{O}H$ combines and aspirin forms sodium salt. Therefore, ionisation of aspirin increases.

94. (2)

1. HOCl, it is S_A. So it is acidic
2. NaOCl, it is salt of NaOH + HOCl (Salt of S_B/W_A).

   $\therefore$ It is basic.
3. $NaHSO_4$ (Salt of S_A/S_B $NaOH + H_2SO_4$), it is neutral
4. NH_4NO_3 (Salt of W_B/S_A $NH_3 + HNO_3$), it is acidic.

95. (1) $pH = pK_a + \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$

$$pH = pK_a + \log\left[\frac{In^{\ominus}}{HIn}\right]$$

$4.3 = pK_a + \log 7$

$pK_a = 4.3 - \log 7$

$pK_a = 4.3 - 0.845 = 3.455$

$K_a = \text{Antilog}(-3.455) = (-3 - 4.55 + 1 - 1)$

$\qquad = \bar{4}.545 = 3.5 \times 10^{-4}$

96. (4) Buffer capacity

$$= \frac{\text{Number of moles per litre of acid or base added}}{\text{Change in pH or pOH}}$$

$$[\text{Acid}] = \frac{0.002 \times 1000}{250} = 0.008 \text{ M}$$

$$\text{Buffer capacity} = \frac{0.008}{0.02} = 0.4$$

97. (1) Since $Ca(OH)_2$ is completely ionised.

	$Ca(OH)_2 \longrightarrow$	Ca^{2+} +	$2\overset{\ominus}{O}H$
Initial	0.1	0	0
Final	0	0.1	$2 \times 0.1 = 0.2M$

BBB Rule: On adding base, to the basic buffer, concentration of base increases and salt decreases.

$\therefore$ New concentration of base and salt are:

$[Base] = [NH_3] = 0.6 + 0.2 = 0.8$ M

$[Salt] = [NH_4Cl] = 0.4 - 0.2 = 0.2$ M

$$\therefore pOH = pK_b + \log\left[\frac{Salt}{Base}\right]$$

$$pOH = 4.74 + \log\left(\frac{0.2}{0.8}\right)$$

$$= 4.74 - 2\log 2 = 4.74 - 2 \times 0.30 = 4.14$$

$pH = 14 - 4.14 = 9.86$

98. (4) Anionic hydrolysis is carried by salts of W_A/S_B, e.g., Na_2CO_3.

99. (1) $Ag_2SO_4 \rightleftharpoons 2Ag^{\oplus} + SO_4^{2-}$

$\qquad\qquad 2x \qquad x$

$K_{sp} = 4x^3 = 4 \times (2.5 \times 10^{-2})^3 = 62.5 \times 10^{-6}$

100. (3) Salt of S_B/W_A are called acid salt.

Na_2S, Na_2SO_3, Na_2SO_4 are salts of S_A/S_B. But $NaHSO_3$ is salt of W_A/S_B.

101. (4) Salt of S_B/W_A are called acid salts.

1. NaH_2PO_4 (Salt of NaOH + H_3PO_4) (S_B/W_A)
2. NaH_2PO_2 (Salt of NaOH + H_3PO_2) (S_B/W_A)
3. NaH_2PO_3 (Salt of NaOH+ H_3PO_3)(S_B/W_A)

All are acid salts.

102. (2) Only salts of S_A/S_B do not hydrolyse while all other salts hydrolyse.

NaCl, KCl, Na_2SO_4 are salts of S_A/S_B, so do not hydrolyse but NH_4Cl is a salt of W_B/S_A and hydrolyses.

103. (1) Similarly like in problem 102(above), $NaNO_3$, KCl and K_2SO_4 are salts of S_A/S_B and do not hydrolyse. But CH_3COOK is a salt of W_A/S_B and hydrolyses.

104. (2) Highest pH will be of the salt of W_A/S_B (pH > 7)

1. NaCl (salt of S_A/S_B, pH = 7)
2. Na_2CO_3 (salt of W_A/S_B, pH > 7)
3. NH_4Cl (salt of S_A/W_B, pH < 7)
4. $NaHCO_3$ (Salt of W_A/S_B, pH > 7)

But (2) and (4) are both salt of W_A/S_B, but the concentration of salt in (2) is more, so pH is more.

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

105. (1)

Since equal volumes are added

1. Ionic product = $\frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = \frac{10^{-8}}{4}$
2. Ionic product = $\frac{10^{-5}}{2} \times \frac{10^{-5}}{2} = \frac{10^{-10}}{4}$
3. Ionic product = $\frac{10^{-5}}{2} \times \frac{10^{-6}}{2} = \frac{10^{-11}}{4}$
4. Ionic product = $\frac{10^{-10}}{2} \times \frac{10^{-10}}{2} = \frac{10^{-20}}{4}$

Only in (a) Ionic product $\left(\frac{10^{-8}}{4}\right) > K_{sp}$ (1.8×10^{-10})

So precipitate will take place only with (a)

106. (3) $[H_3O^{\oplus}] = 0.01 = 10^{-2}$ M

$pH = -\log(10^{-2}) = 2$

107. (1) Stronger is the acid, weaker is the conjugate base and vice versa.

Base	**Acid**
$ClO^{\ominus}$	HClO
$ClO_2^{\ominus}$	$HClO_2$
$ClO_3^{\ominus}$	$HClO_3$
$ClO_4^{\ominus}$	$HClO_4$

Acidic order: $HClO_4 > HClO_3 > HClO_2 > HClO$

Conjugate base order: $ClO_4^{\ominus} < ClO_3^{\ominus} < ClO_2^{\ominus} < ClO^{\ominus}$

$\therefore$ Strongest base = $ClO^{\ominus}$

108. (2)

	$CH_3COOH + H_2O \rightleftharpoons$	$CH_3COO^{\ominus}$ +	$H_3O^{\oplus}$
Intial	1	0	0
Final	$C(1-\alpha)$	$C\alpha$	$C\alpha$

C = Decinormal = 0.1 N

$$\alpha = 1.3\% = \frac{1.3}{100} = 1.3 \times 10^{-2}$$

$[H_3O^{\oplus}] = C\alpha = 0.1 \times 1.3 \times 10^{-2} = 1.3 \times 10^{-3}$

$pH = -\log(1.3 \times 10^{-3}) = -\log 1.3 - \log 10^{-3}$

$= -0.11 + 3 = 2.89$

109. (1) $Al_2(SO_4)_3$ is a salt of W_B/S_A. $[Al(OH)_3 + H_2SO_4]$. It hydrolyses and gives acidic solution.

110. (1) Salt of W_B/S_A hydrolyses and is called cation hydrolysis.

111. (3) NaOH = 10 × 0.1 = 1 mEq

Na_2SO_4 = 10 × 0.05 = 0.5 mEq

But pH of solution is due to only strong base, NaOH and will be greater than 7. Salt of S_A/S_B, has no effect on pH, since its pH is 7.

112. (2) HCl = 20 × 0.1 = 2 mEq

KOH = 20 × 0.1 = 2 mEq

2 mEq HCl combines with 2 mEq of KOH and forms KCl, a salt of S_A/S_B which do not hydrolyses and gives neutral solution with pH = 7.

113. (1) Salt of S_B/W_A will be basic.

1. Sodium borate, salt of S_B/W_A (NaOH + H_3BO_3). It gives basic solution.
2. NH_4Cl, salt of W_B/S_A, (NH_4OH + HCl). It hydrolyses and gives acidic solution.
3. $Ca(NO_3)_2$, salt of W_B/S_A. [$Ca(OH)_2 + HNO_3$), and gives acidic solution.

4. Na_2SO_4, salt of S_A/S_B, which do not hydrolyses, gives neutral solution with pH = 7.

114. (2) $AgBr \longrightarrow Ag^{\oplus} + Br^{\ominus}$

1. $NaBr \longrightarrow Na^{+} + Br^{\ominus}$

   Due to common ion effect of $Br^{\ominus}$, solubility of AgBr will be less.

2. $NH_4OH \longrightarrow NH_4^{\oplus} + \overset{\ominus}{O}H$

   $Ag^{\oplus} + \overset{\ominus}{O}H \longrightarrow AgOH$

   $\overset{\ominus}{O}H$ combines with $Ag^{\oplus}$ ions to give AgOH. So according to Le Chatelier's principle, reaction will proceed in forward direction and hence solubility of AgBr in H_2O will increase.

3. Solubility of AgBr in H_2O will remain unaffected (here $\overset{\ominus}{O}H$ from water is very less i.e., $[\overset{\ominus}{O}H] = 10^{-7}$)

4. $HBr \longrightarrow H^{\oplus} + Br^{\ominus}$

   So again due to common ion effect of $Br^{\ominus}$, solubility of AgBr will decrease.

115. (4)

1. $HCl = 100 \times \frac{1}{10} = 10\text{ mEq}$

   $NaOH = 100 \times \frac{1}{10} = 10\text{ mEq}$

   Salt of S_A/S_B is formed, pH = 7.

2. $HCl = 55 \times \frac{1}{10} = 5.5\text{ mEq}$

   $NaOH = 45 \times \frac{1}{10} = 4.5\text{ mEq}$

   1.0 mEq of HCl is left. So pH will be in acidic range but not equal to one, since concentration of HCl is very low.

3. $HCl = 10 \times \frac{1}{10} = 1\text{ mEq}$

   $NaOH = 90 \times \frac{1}{10} = 9\text{ mEq}$

   8 mEq of NaOH is left and pH > 7.

4. $HCl = 75 \times \frac{1}{5} = 15\text{ mEq}$

   $NaOH = 25 \times \frac{1}{5} = 5\text{ mEq}$

   15 – 5 = 10 mEq of HCl is left.

   $$\therefore [HCl] = [H_3O^{\oplus}] = \frac{10\text{ mEq}}{(75+25)\text{ mL}} = \frac{10}{100} = 0.1\text{ M}$$

   $pH = -\log(10^{-1}) = 1.$

116. (3) Decrease or increase in the concentration of CO_2 does not effect pH.

117. (4)

1. Acidic buffer, and have pH < 7
2. Also acidic buffer, pH < 7
3. Salt of W_A/W_B, pH = 7
4. Basic buffer, and pH > 7.

118. (2) Most soluble compound is that which have highest K_{sp} value. K_{sp} of MnS (7×10^{-6}) is highest.

119. (3) Let the initial concentration of $H^{\oplus} = 10^{-1}M$

pH = 1

The new concentration of $H^{\oplus}$, is 10 times the initial concentration of $H^{\oplus} = 10 \times 10^{-1}\text{ M} = 10^{\circ} = 1$

$pH_2 = -\log(1) = 0$

The change in $pH = pH_1 - pH_2 = 1.0 = 0$

Change in pH is one and it decreases from 1 to zero.

120. (3) The dissociation constants of weak acid and its conjugate base are related by an expression.

$pK_a + pK_a - pK_w$

i.e. $pK_a + 10.83 = 14$

or $pK_a = 14 - 10.83 = 3.17$

or $K_a = \text{antilog}(-3.17) = 6.76 \times 10^{-4}$

121. (4) Factual statement.

Multiple Correct Answers Type

1. **(1, 3)**

$$CH_3NH_2 + HCl \longrightarrow CH_3\overset{\oplus}{N}H_3 + Cl^{\ominus}$$

	CH_3NH_2	HCl	$CH_3\overset{\oplus}{N}H_3$	$Cl^{\ominus}$
Initial moles	0.1	0.08		
Final	(0.1–0.08) = 0.02	(0.008–0.008) = 0	0.008	–

Since W_B is left, so it forms basic buffer solution

$$[\overset{\ominus}{O}H] = K_b\frac{[\text{Base}]}{[\text{Salt}]} = 5 \times 10^{-4} \times \frac{0.02}{0.08} = 1.25 \times 10^{-4}$$

$$[H^{\oplus}] = \frac{K_w}{[\overset{\ominus}{O}H]} = \frac{10^{-14}}{1.25 \times 10^{-4}} = 8 \times 10^{-11}M$$

$pH = -\log(8 \times 10^{-11})$

$= -\log 2^4 + 11$

$= -0.3 \times 4 + 11 = 9.8$

$pOH = 14 - 9.8 = 4.2$

2. **(2, 3, 4)**

   (1) is wrong.

   For reaction of S_A with W_B, basic buffer is formed β is maximum. When $pOH = pK_b$.

   At 50% neutralisation (25 mL of 0.1 N HCl)

   Slope of the given graph will be least and the buffer will have maximum buffer capacity

3. **(1, 2)** Factual statements

4. **(1, 2)** $\underset{\text{Red}}{HIn} \rightleftharpoons \underset{\text{Blue}}{Ind^{\ominus}} + H^{\oplus}\ (pK_a = 5)$

   1. when $pH < pK_a$ (4.52 < 5), colour of acid form, i.e., red predominates.
   2. when $pH > pK_a$ (5.47 > 5), colour of basic form, i.e., blue predominates.
   3. 75% red $\Rightarrow \left[\frac{In^{\ominus}}{HIn}\right] = \frac{0.75}{0.25}$

$\Rightarrow$ pH = 5 + log 3 = 5 + 0.48 = 5.48 (Hence (c) is wrong)

(4) is also wrong statement.

5. **(1, 2, 4)** Factual statement.

6. **(1)**

i. $$\text{Ag}_2\text{SO}_4 \rightleftharpoons \underset{2x}{2\text{Ag}^{\oplus}} + \underset{x}{\text{SO}_4^{2-}}$$

ii. $$\text{BaSO}_4 \rightleftharpoons \underset{y}{\text{Ba}^{2+}} + \underset{y}{\text{SO}_4^{2-}}$$

iii. $$\text{Ba}_3(\text{PO}_4)_2 \rightleftharpoons \underset{3z}{3\text{Ba}^{2+}} + \underset{2z}{2\text{PO}_4^{3-}}$$

$\therefore [\text{Ag}^{\oplus}] = 2x$, $[\text{SO}_4^{2-}] = x + y$, $[\text{Ba}^{2+}] = x + 3z$;
$[\text{PO}_4^{3-}] = 2z$

Direct method: By electroneutrality.

$$\left[\begin{array}{c}\text{Total positive charge} = \text{Total negative charge}\\ \text{Total charge} = \text{Charge on the ion} \times \text{Concentration}\end{array}\right]$$

iv. $1 \times [\text{Ag}^{\oplus}] + 2[\text{Ba}^{2+}] = 2[\text{SO}_4^{2-}] + 3[\text{PO}_4^{3-}]$

Alternatively: Substituting the concentration of each ion in (iv).

$$2x + 2(x + 3z) = 2\,(x + y) + 3\,(2z)$$

Dividing by 2: $x + (x + 3z) = (x + y) + \frac{3}{2}(2z)$

$$\frac{[\text{Ag}^{\oplus}]}{2} + [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] + \frac{3}{2}[\text{PO}_4^{3-}]$$

or

$[\text{Ag}^{\oplus}] + 2[\text{Ba}^{2+}] = 2[\text{SO}_4^{2-}] + 3[\text{PO}_4^{3-}]$

Hence answer is (1)

7. **(4)** For precipitation, $[\text{Ag}^{\oplus}]$ ion should be minimum in the solution.

For AgCl: $$[\text{Ag}^{\oplus}]_{\min} = \frac{K_{sp}\ \text{AgCl}}{[\text{Cl}^{\ominus}]} = \frac{1.5 \times 10^{-10}}{1.5 \times 10^{-1}} = 10^{-9}\text{M}$$

For AgBr: $$[\text{Ag}^{\oplus}]_{\min} = \frac{K_{sp}\text{AgBr}}{[\text{Br}^{\ominus}]} = \frac{5.0 \times 10^{-13}}{5.0 \times 10^{-4}} = 10^{-9}\text{M}$$

For Ag_2CrO_4: $[\text{Ag}^{\oplus}]_{\min}$

$$= \left(\frac{K_{sp}\ \text{Ag}_2\text{CrO}_4}{[\text{CrO}_4^{2}]}\right)^{\frac{1}{2}} = \left(\frac{1.9 \times 10^{-12}}{1.9 \times 10^{-2}}\right) = 10^{-5}\,\text{M}$$

Therefore, $[\text{Ag}^{\oplus}]$ min in solution is in AgCl and AgBr, so both will be precipitated.

8. **(2)** $\text{Hg}_2\text{CrO}_4 \rightleftharpoons \text{Hg}_2^{2+} + \text{CrO}_4^{2-}$

$[\text{Hg}_2^{2+}] = 4 \times 10^{-4}$ M, $[\text{CrO}_4^{2-}] = 2 \times 10^{-5}$

$K_{sp} = (4 \times 10^{-4})\,(2 \times 10^{-5}) = 8 \times 10^{-9}$

9. **(2, 4)**

1. **Wrong:** Indicator should have a small transition range.
2. **Correct:** pH at equivalence point $\approx \text{pH}_{\text{Ind}}$
3. **Wrong:** pH at equivalence point and at the end point may be different.
4. **Correct:** Factual statement.

10. **(2, 4)**

1. Wrong statement.
2. **Correct:** Indicators are weak acid or base and are added is small amount. So they do not affect the pH of the solution.
3. **Wrong:** They occur even in the absence of indicators.
4. **Correct:** Factual statement.

11. **(1, 2)**

$pK_a = -\log(3 \times 10^{-5}) = -0.48 + 5 = 4.52$

$$\text{H}_{\text{Ind}} \rightleftharpoons \text{Ind}^{\ominus} + \text{H}^{\oplus}$$

	(Red)	(Blue)
(i)	75%	25%
(ii)	25%	75%

(i) $$\text{pH} = 4.52 + \log\left(\frac{25}{75}\right) = 4.52 + \log\frac{1}{3} = 4.52 - 0.48 = 4.04$$

(ii) $$\text{pH} = 4.52 + \log\left(\frac{75}{25}\right) = 4.52 + 0.48 = 5.0$$

12. **(1, 2)**

1. **Correct:** At the point, $[\text{H}^{\oplus}]$ becomes small and to change it, small amount of $[\overset{\ominus}{\text{O}}\text{H}]$ is required. When $[\text{H}^{\oplus}]$ changes from 10^{-6} M to 10^{-7} M, pH change is one, but the volume of NaOH required for this change is very small. So, the curve changes sharply.
2. **Correct:** Quinoid structure is obtained.
   [Refer solution of Q. 12, Single Correct Answer Type]
   (3) and (4) are wrong statements.

13. **(3)**

1. For the titration of W_A and W_B, there is no sharp change in the pH value near the end point.
   (pH varies between 6.0 and 8.0)
   So indicator V can not be used. But indicator X can be used.
   $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \Rightarrow \text{pH} = 7$
2. $$\left.\begin{array}{r}0.1\text{ M NaOH} \Rightarrow \text{pH} = 13\\ 0.001\text{ M NaOH} \Rightarrow \text{pH} = 11\end{array}\right]$$
   Y cannot be used. Choose an indicator which has different colour for pH = 13 and 11.
3. X can be used since it will give different colour in both the solutions. NH_4Cl (Salt of W_B/S_A pH < 7) and CH_3COONa (salt of W_A/S_B pH > 7).
4. Y will be suitable indicator not W.
   $\text{CH}_3\text{COOH} + \text{Base} \Rightarrow \text{pH} > 7.$

14. **(2, 4)**

1. Statement (1) is correct.
   K_a values decreases successively, since it is difficult to remove $\text{H}^{\oplus}$ ion from an anion than a neutral compound. Similarly, it is difficult to remove $\text{H}^{\oplus}$ ion from an ionian than and anion.

Hence $K_{a_1} > K_{a_2} > K_{a_3}$

2. Statement (2) is incorrect.

$$H_3PO_4 \overset{K_{a_1}}{\rightleftharpoons} H^{\oplus} + H_2PO_4^{\ominus}$$

$$H_3PO_4^{\ominus} \overset{K_{a_2}}{\rightleftharpoons} H^{\oplus} + HPO_4^{2-}$$

$$pH(H_2PO_4^{\ominus}) = \frac{pK_{a_1} + pK_{a_2}}{2}$$

This is valid only when H_3PO_4 during titration is completely converted to $H_2PO_4^{\ominus}$.

$$HPO_4^{2-} \overset{K_{a_3}}{\rightleftharpoons} H^{\oplus} + PO_4^{3-}$$

$$pH(HPO_4^{2-}) = \frac{pK_{a_2} + pK_{a_3}}{2}$$

This is again valid when starting with $H_2PO_4^{2-}$ and is completely converted to HPO_4^{2-}.

3. Statement (3) is correct.

From the K_a values, it is evident that

both H_3PO_4 and $H_2PO_4^{\ominus}$ are more acidic than HPO_4^{2-}.

4. Statement (4) is incorrect.

Both $H_2PO_4^{\ominus}$ and HPO_4^{2-} are amphiprotic anion in the solution.

$$H_3PO_4 \xleftarrow{+H^{\oplus}} H_2PO_4^{\ominus} \xrightarrow{-H^{\oplus}} HPO_4^{2-} + H^{\oplus}$$

$$H_2PO_4^{\ominus} \xleftarrow{+H^{\oplus}} HPO_4^{2-} \xrightarrow{-H^{\oplus}} PO_4^{3-} + H^{\oplus}$$

15. (1, 2, 3)

Since concentrations are identical

If V_1 is the volume of CH_3COOH and V_2 is the volume of NaOH.

1. $CH_3COOH + NaOH$] Buffer is formed if $V_1 > V_2$

V_1 V_2

$M_1 \approx M_2$

mmol of CH_3COOH (M_1V_1) > mmol of NaOH (M_2V_2).
So W_A is left and buffer is formed.

2. $CH_3COOK + HNO_3 \longrightarrow CH_3COOH + KNO_3$]

V_1 V_2

$M_1 \approx M_2$

Buffer is formed $V_1 > V_2$

mmol of salt (CH_3COOK) > mmol of HNO_3. Some salt is hydrolysed to give CH_3COOH and some salt CH_3COOK is left to give buffer solution. KNO_3 is completely ionised.

3. $CH_3COOH + CH_3COOK$]

V_1 V_2

Forms always a buffer. Mixture of W_A and salt of W_A/S_B.

4. $HNO_3 + CH_3COOH$] It is a mixture of S_A and W_A

16. (1, 3)

Addition of H_2O will not change pH only for buffer solution. (Buffer is formed if W_A or W_B is left after neutralisation)

1. **Acid buffer:** $CH_3COOH = 100 \times 0.2 = 20$ mmol

NaOH = $100 \times 0.1 = 10$ mmol

10 mmoles of CH_3COOH will react with 10 mmol of NaOH to form 10 mmol of CH_3COONa and 10 mmol of CH_3COOH is left.

2. mmol of $CH_3COOH = 100 \times 0.2 = 20$

mmol of NaOH $= 100 \times 0.2 = 20$

(Salt of W_A/S_B is formed.)

3. mmol of $CH_3COOH = 200 \times 0.2 = 40$

mmol of NaOH $= 100 \times 0.1 = 10$

mmol of CH_3COOH left $= 40 - 10 = 30$.

mmol of CH_3COONa formed $= 10$.

(Buffer is formed)

4. mmol of $CH_3COOH = 100 \times 0.2 = 20$

mmol of NaOH $= 200 \times 0.2 = 40$

mmol of NaOH left $= 40 - 20 = 20$

S_B is left.

17. (1, 2, 3)

Salt of W_B/S_A have pH > 7.

Note: Salt of W_A/W_B have pH < 7 if acidic part is stronger i.e., if $pK_b > pK_a$.

1. $NH_4F \equiv NH_3 + HF$ $(K_a > K_b$ or $pK_b > pK_a)$

W_B W_A (pH < 7)

2. $Cr(NO_3)_3 \equiv Cr(OH)_3 + HNO_3$ [$pH < 7$]

W_B S_A

3. $[(CH_3)_3NH]Cl \equiv (CH_3)_3\overset{\oplus}{NH}\overset{\ominus}{OH} + HCl$ (pH > 7)

W_B S_A

4. $CaI_2 \equiv Ca(OH)_2 + HI$ (pH = 7)

S_B S_A

18. (1, 3)

1. Cationic hydrolysis:

$$B^{\oplus} + H_2O \longrightarrow \underset{W_B}{BOH} + H^{\oplus}$$

$B^{\oplus}$ accepts $\overset{\ominus}{OH}$ from H_2O

3. Anionic hydrolysis:

$$A^{\ominus} + H_2O \longrightarrow \underset{W_A}{HA} + \overset{\ominus}{OH}$$

$A^{\ominus}$ accepts $H^{\oplus}$ from H_2O

19. (1, 2)

Either buffer or salt of W_A/W_B solutions pH values does not change on dilution.

Since in buffer, on dilution both the concentration of W_A or W_B and their conjugate ions change, but their ratio remains same.

Hydrolysis of salts of W_A/W_B are independent on the concentration, so their pH values also does not change on dilution.

20. (1, 3)

For any polyprotic acid: $K_{a1} > K_{a2} > ....$ and so on.

21. (2, 3, 4)

Salt of S_A and W_B: $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \cdot C}}$

$\Rightarrow h$ increases as 'C' decreases [on dilution]

As T increases, K_h increases $\Rightarrow$ h increases.

As T decreases, K_h decreases $\Rightarrow$ h decreases.

As strength of base decreases (i.e., K_b decreases) $\Rightarrow$ h increases

Note: Both K_w and K_b increase with increase in temperature, but K_w will increase sharply as compared to K_b. So K_h increases with increase in temperature.

22. (1, 2, 4)

NaCl + NaI

0.05 M 0.05 M

When $AgNO_3$ is added, find the minimum concentration of $Ag^{\oplus}$ required to start precipitation.

$$[Ag^{\oplus}]_{AgCl} = \frac{K_{sp(NaCl)}}{[Cl^{\ominus}]} = \frac{10^{-10}}{0.05} = 2 \times 10^{-9} \text{ M}$$

$$[Ag^{\oplus}]_{AgI} = \frac{K_{sp(AgI)}}{[I^{\ominus}]} = \frac{4 \times 10^{-16}}{0.05} = 8 \times 10^{-15} \text{ M}$$

Since, there is a very high difference between the minimum concentrations of $Ag^{\oplus}$, precipitation is selective and AgI will precipitate first.

23. (2, 4)

$MgCl_2$ + NaF [After dilution]

7.5×10^{-4} M 1.25×10^{-2} M

I.P. of $MgF_2 = [Mg^{2+}][F^{\ominus}]^2$

$= (7.5 \times 10^{-4})(1.25 \times 10^{-2})^2 > K_{sp(MgF_2)}$

$\Rightarrow MgF_2$ will get precipitated and $Cl^{\ominus}$ ions will remain in solution.

24. (2, 3)

Acidic buffer: $pH = pK_a + \log \frac{[Salt]}{[Acid]}$ If more salt is added, pH increases.

Basic buffer: $pOH = pK_b + \log \frac{[Salt]}{[Base]}$ If more salt is added, pOH increases or pH decreases.

25. (1, 2, 4)

For acidic buffer, buffer capacity is maximum at pH = pK_a and for basic buffer, it is maximum at pH = $pK_w - pK_b$.

Buffer is always effective within a pH range of 1 with respect to the pH at maximum buffer capacity.

$H_3PO_4 + H_2PO_4^{\ominus}$ is a buffer solution.

26. (1, 2, 3, 4)

Calculation of molecular weight of BOH:

Eq of base = Eq of H_2SO_4 used

$$\frac{0.496 \text{ g}}{Mw \text{ of base}} \times 1 = 40 \times 10^{-3} \times \frac{1}{2} \times 2 (n \text{ factor})$$

$\therefore$ Mw of BOH = 12.4 g mol^{-1}

Now: $\Delta_f T = iK_f m$

$$0.165 = i \times 1.86 \times \frac{1.5}{12.4} \times \frac{1000}{150} = i \times 1.86 \times 0.8$$

(So m = 0.8)

$$\therefore i = \frac{0.165 \times 12.4}{1.86} = 1.1$$

For weak base: $1 + \alpha = 1.1, \Rightarrow \alpha = 0.1 = 10\%$(Answer d)

Thus, $[\overset{\ominus}{O}H] = C\alpha = 0.8 \times 0.1 = 8 \times 10^{-2}$,

$\therefore$ pOH = 1.1, pH = 12.9 (Answer a)

So, $K_b = C\alpha^2 = 0.8 \times (0.1)^2 = 8 \times 10^{-3}$, (Answer b)

Also; $\pi = iMRT$

$= 1.1 \times 0.8 \times 0.0821 \times 300$

$= 21.67$ atm (Answer 3)

27. (2, 3)

$$K_1K_2 = \frac{[H^{\oplus}]^2[S^{2-}]}{[H_2S]} = 10^{-21}$$

Note: Saturated H_2S means 0.1 M H_2S.

i. $$\frac{(0.2)^2/[S^{2-}]}{0.1} = 10^{-21}$$

$$\therefore [S^{2-}] = \frac{10^{-22}}{0.04} = 2.5 \times 10^{-21}$$

$K_{sp} = [Fe^{2+}][S^{2-}] = 3.7 \times 10^{-19}$.

Since $(0.01)(2.5 \times 10^{-21}) < 3.7 \times 10^{-19}$

FeS will not precipitate.

ii. $$\frac{(0.001)^2/[S^{2-}]}{0.1} = 10^{-21}, \quad [S^{-2}] = 10^{-16}.$$

Since $(0.01)(10^{-16}) < 3.7 \times 10^{-19}$

Fes will precipitate.

28. (1, 2, 3)

29. (1, 2, 3, 4) All factual statements

30. (1, 2, 3)

1. $$M = \frac{W_2 \times 1000}{Mw_2 \times V_{sol}(\text{in mL})} = \frac{2 \times 1000}{40 \times 500} = 0.1 \text{ M}$$

$\therefore [NaOH] = [\overset{\ominus}{O}H] = 0.1 = 10^{-1}$ M

pOH = 1, pH = 13

2. 0.05 M $Ca(OH)_2$ = 2 × 0.05 N $Ca(OH)_2$

$\therefore [\overset{\ominus}{O}H] = 2 \times 0.05 = 0.1 = 10^{-1}$ M

pOH = 1 pH = 13

3. 100 mL of 0.1 N $Ca(OH)_2$,

$\therefore [\overset{\ominus}{O}H] = 0.1 \text{ N} = 10^{-1}$ M

pOH = 1 pH = 13

4. $$M = \frac{4 \times 1000}{40 \times 500} = \frac{1}{5} = 0.2 \text{ M}$$

$[\overset{\ominus}{O}H] = 0.2$ M

$\text{pOH} = -\log[0.2] = -\log 2 + \log 10 = -0.3010 + 1$

$= 0.699$

$\text{pH} = 14 - 0.699 = 13.301$

So the answer (1), (2), and (3) are correct.

31. (2, 3) Self-explanatory.

32. (2) The characteristics of the given solutions are:

NaCl Neutral solution (Salt of S_A/S_B)

NH_4Cl Slightly acidic due to the reaction (Salt of W_B/S_A)

$$NH_4^{\oplus} + H_2O \rightleftharpoons NH_4OH + H^{\oplus}$$

NaCN Slightly alkaline due to the reaction (Salt of S_B/W_A)

$$CN^{\ominus} + H_2O \rightleftharpoons HCN + OH$$

HCl highly acidic

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline.

i.e., $HCl < NH_4Cl < NaCl < NaCN$

33. (1, 3)

A buffer solution is obtained by mixing a weak acid/base with salt of its conjugate base/acid.

Linked Comprehension Type

1. (2) $\underset{\substack{0.8 \times 15 \\ = 12}}{2KIO_3} + \underset{\substack{35 \times 0.15 \\ = 5.25}}{Pb(NO_3)_2} \longrightarrow Pb(IO_3)_2 + 2KNO_3$

1 mol of $Pb(NO_3)_2$ reacts with 2 mol of KIO_3.

5.25 mmol of $Pb(NO_3)_2$ reacts $= 2 \times 5.25 = 10.5$ mmol

mmol of KIO_3 left $= 12 - 10.5 = 1.5$.

Hence $Pb(NO_3)_2$ is the limiting reactant.

2. (4) $[IO_3^{\ominus}] = \dfrac{1.5 \text{ mmol}}{(15+35)\text{ mL}} = 0.03 \text{ M}$

3. (3) Due to common ion ($IO_3^{\ominus}$) left in the solution, the solubility $Pb(IO_3)_2$ decreases

$$S = \frac{K_{sp}}{(0.03)^2} = \frac{2.6\times10^{-13}\times10^4}{9}$$

$$= 0.28 \times 10^{-9} = 2.8 \times 10^{-10}$$

4. (2) (1) and (3) are not true since at equivalence point, they represent neutral solution.

(4) is clearly wrong, since, $K_w = [H^{\oplus}]\,[\overset{\ominus}{O}H]$

(2) is correct.

5. (4) $pK_a = -\log(4 \times 10^{-4}) = -2\log 2 + 4$

$= -2 \times 0.3 + 4 = 3.4$

$pK_a > \text{pH}$ $(3.4 > 2)$

At $pH < pK_a$, the system moves to the left to give HMO, hence the colour is red.

6. (2) Since K_{a_1} and K_{a_2} are high values therefore point A, K_{a_1} and K_{a_2} are considered.

$$H_3A \rightleftharpoons H^{\oplus} + H_2A^{\ominus}$$

$$H_2A^{\ominus} \rightleftharpoons H^{\oplus} + HA^{2-}$$

$$K_{a_1} \times K_{a_2} = \frac{[H^{\oplus}][HA^{2-}]}{[H_3A]} \quad \left[\begin{array}{c}\text{At equivalence point} \\ [HA^{2-}] = [H_3A]\end{array}\right]$$

$$-\log K_{a_1} - \log K_{a_2} = -2\log[H^{\oplus}]$$

$$pK_{a_1} + pK_{a_2} = 2\text{pH}.$$

$$\therefore \text{pH} = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{3+5}{2} = 4$$

7. (3) At point C, Na_3A is formed, hydrolysis of A^{3-} occurs and hydrolysis of Na_2HA is suppressed, (K_{a_3} is considered) due to common ion $[\overset{\ominus}{O}H]$ effect

$$A^{3-} + H_2O \rightleftharpoons HA^{2-} + \overset{\ominus}{O}H$$

$$HA^{2-} + H_2O \rightleftharpoons H_2A^{\ominus} + \overset{\ominus}{O}H$$

At point *C* salt Na_3A (salt of W_A/S_B) is formed. Since the concentration of NaOH and H_3A (0.1) are equal. So the volume of NaOH used at point C is 3 times the volume of H_3A used.

Total volume of solution = 100 mL (H_3A) + 300 mL (NaOH) = 400 mL.

$M_1V_1(\text{Before}) = M_2V_2\,(\text{After})$

$0.1 \times 100 = M_2 \times 400$

$$M_2 = \frac{0.1}{4} = 0.025$$

Hence the concentration of salt (Na_3A) formed at point C = 0.025.

Using hydrolysis equation for N_3A (using K_{a_3} value).

$$\text{pH} = \frac{1}{2}(pK_w + pK_{a_3} + \log C)$$

$$= \frac{1}{2}(14 + 7 + \log 25 \times 10^{-3}) = \frac{1}{2}(21 - 1.6) = 9.7$$

$\therefore \text{pH} = 9.7$

8. (4) At point B, Na_2HA is formed, hydrolysis of HA^{2-} is considered and hydrolysis of NaH_2A is suppressed (K_{a_2} is considered) due to common ion $[\overset{\ominus}{O}H]$ effect.

$$HA^{2-} + H_2O \rightleftharpoons H_2A^{\ominus} + \overset{\ominus}{O}H$$

$$H_2A^{\ominus} + H_2O \rightleftharpoons H_3A + \overset{\ominus}{O}H$$

At point B, salt Na_2HA (salt of W_A/S_B) is formed. So the volume of NaOH used at point B is 2 times the volume of H_3A used.

Total volume of solution

= (100 mL + 200 mL) = 300 mL

$M_1V_1(\text{Before}) = M_2V_2\,(\text{After})$

$0.1 \times 100 = M_2 \times 300$

$$M_2 = \frac{0.1}{3} = \frac{1}{30} = 0.033$$

$\therefore [Na_2HA] = 0.033$ M

$$\therefore \text{pH} = \frac{1}{2}(pK_w + pK_{a_3} + \log C)$$

$$= \frac{1}{2}\left(14+5+\log\frac{1}{30}\right) = \frac{1}{2}(19-1.48) = 8.76$$

change is pH = 9.7 − 8.76 = 0.94

9. **(3)** $[S^{2-}]_{\min}$ for SnS $= \dfrac{K_{sp}\,(SnS)}{[Sn^{2+}]}$;

$[S^{2-}]_{\min}$ for CdS $= \dfrac{K_{sp}\,(CdS)}{[Cd^{2+}]}$;

$[S^{2-}]_{\min}$ for NiS $= \dfrac{K_{sp}\,(NiS)}{[Ni^{2+}]}$;

and $K_{sp}\,(NiS) < K_{sp}\,(SnS) < K_{sp}\,(CdS)$

∴ NiS will precipitate first.

10. **(3)** $H_2S \longrightarrow 2H^{\oplus} + S^{2-} \Rightarrow K_1K_2 = \dfrac{[H^{\oplus}]^2\,[S^{2-}]}{[H_2S]} = 10^{-21}$

$$[S^{2-}] = \frac{K_{sp}\,(NiS)}{[Ni^{2+}]} = \frac{3\times10^{-21}}{0.1} = 3\times10^{-20}$$

$$\frac{[H^{\oplus}]^2\,(3\times10^{-20})}{0.1} = 10^{-21},\ [H^{\oplus}] = \left(\frac{10^{-21}\times0.1}{3\times10^{-20}}\right)^{\frac{1}{2}}$$

$$= \sqrt{0.33}\times10^{-1} = 5.74\times10^{-2}$$

pH = 1.24

11. **(1)** Solubility of either CdS, NiS, SnS = $\sqrt{K_{sp}}$ ⇒ look for highest K_{sp}.

CdS is more soluble.

12. **(1)** $K_1K_2 = \dfrac{[H^{\oplus}]^2\,[S^{2-}]}{[H_2S]} \Rightarrow [S^{2-}]_{\min} = 10^{-20}$ M

$$\Rightarrow [Cd^{2+}]_{\text{allowed}} = \frac{K_{sp}\,(CdS)}{[S^{2-}]_{\text{salt}}} = 10^{-8}\,\text{M}$$

13. **(1)** Use: $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{C_2}{C_1}} \Rightarrow \dfrac{4.24}{\alpha_2} = \sqrt{\dfrac{0.1}{0.01}}$

$$\Rightarrow \alpha_2 = \frac{4.24}{\sqrt{10}}\% = 1.33\%$$

14. **(1)** pH of 0.005 M HCOOH : $K_a = 2\times10^{-4}$

Since C is low and K_a is high. Solve the quadratic equation:

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

$$\Rightarrow 2\times10^{-4} = \frac{(0.005)\alpha^2}{1-\alpha} \quad \Rightarrow \quad \alpha = 0.18$$

$$\Rightarrow \text{pH} = -\log C\alpha = -\log(0.005\times0.18) \approx 3$$

15. **(1)** $\dfrac{\alpha_1}{\alpha_2} = \dfrac{1}{2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}} \Rightarrow K_{a_2} = 4K_{a_1} = 8\times10^{-4}$

For Problems 16–18

On dilution (equal volume) and if there were no precipitation.

$[NO_3^{\ominus}] = [Ag^{\oplus}] = [Cl^{\ominus}] = [Br^{\ominus}] = \dfrac{0.01}{2} = 0.005\text{ M} = 5.0\times10^{-3}$ M.

AgBr is the more soluble salt (less K_{sp} means more soluble) and would take precedence in the precipitating reaction.

Assume AgCl does not precipitate. In this case $Ag^{\oplus}$ and $Br^{\ominus}$ would be removed by precipitation and the concentration of these two ions in solution would remain equal to each other.

$$[Ag^{\oplus}] = [Br^{\ominus}] = \sqrt{K_{sp}\ AgBr} = (5.0\times10^{-13})^{\frac{1}{2}}$$

$$= 7.1\times10^{-7}\ \text{M}.$$

Q_{sp} or I.P. of AgCl = $[Ag^{\oplus}]\,[Cl^{\ominus}]$

$= (7.1\times10^{-7})\,(5.0\times10^{-3}\text{ M}) = 3.5\times10^{-9}$

Q_{sp} of AgCl > K_{sp} of AgCl. (∴ Some AgCl most also precipitate)

Hence the assumption is wrong.

Since both halides precipitate, it is a case of simultaneous solubilities.

By electroneutrality

$[Na^{\oplus}] + [Ag^{\oplus}] = [Cl^{\ominus}] + [Br^{\ominus}] + [NO_3^{\ominus}]$

$0.01 + [Ag^{\oplus}] = [Cl^{\ominus}] + [Br^{\ominus}] + 0.005$

or $[Cl^{\ominus}] + [Br^{\ominus}] - [Ag^{\oplus}] = 0.005.$ ...(i)

$[Ag^{\oplus}]\,[Cl^{\ominus}] = 10^{-10}$ ...(ii)

$[Ag^{\oplus}]\,[Br^{\ominus}] = 5\times10^{-13}$ ...(iii)

Divide (ii) by (iii), $\dfrac{[Cl^{\ominus}]}{[Br^{\ominus}]} = 200$

This shows $Br^{\ominus}$ plays a significant role in the total anion concentration of the solution.

Moreover, $[Ag^{\oplus}]$ must be negligible in (i) because of insolubility of two silver salts.

Therefore assume in (i) that $[Cl^{\ominus}] = 0.005 = 5\times10^{-3}$.

16. **(3)** $[Cl^{\ominus}] = 5\times10^{-3}$

From (ii),

$$[Ag^{\oplus}] = \frac{10^{-10}}{[Cl^{\ominus}]} = \frac{10^{-10}}{0.005} = 2.0\times10^{-8}$$

17. **(1)** $[Ag^{\oplus}] = 2.0\times10^{-8}$.

From (iii),

$$[Br^{\ominus}] = \frac{5.0\times10^{-13}}{[Ag^{\oplus}]} = \frac{5.0\times10^{-13}}{2.0\times10^{-8}} = 2.5\times10^{-5}$$

18. **(3)** $[Br^{\ominus}] = 2.5\times10^{-5}$

Check of assumption: Both $[Ag^{\oplus}]$ and $[Br^{\ominus}]$ are negligible compared with $[Cl^{\ominus}]$ of 0.005 M.

For Problems 19–21

$$CuCl_2.2H_2O \longrightarrow Cu^{2+} + 2Cl^{\ominus} + 2H_2O$$

	Cu^{2+}	+	$Cl^{\ominus}$	$\longrightarrow$	$CuCl^{\oplus}$
Initial mol	1.5		2×1.5 = (3.0)		0
At equilibrium	1.5 − x		3.0 − x		x

$$K_f = \frac{[CuCl^{\oplus}]}{[Cu^{2+}][Cl^{\ominus}]} = 1.0$$

$$\Rightarrow \frac{x}{(1.5-x)\,(3.0-x)} = 1.0$$

$\Rightarrow x = 4.5 - 4.5x + x^2$

$\Rightarrow x^2 - 5.5x + 4.5 = 0$

$$x = \frac{5.5 \pm \sqrt{(5.5)^2 - 4(4.5)}}{2}, \quad x = 1.0 \text{ or } 4.5$$

19. **(1)** $[Cu^{2+}] = 0.5$ M

20. **(1)** $[Cl^{\ominus}] = 2.0$ M

21. **(2)** $[CuCl^{\oplus}] = 1.0$ M

22. **(3)** By Henry's law:

$p_{CO_2} = x_{CO_2} K_H$

$$x_{CO_2} = \frac{p_{CO_2}}{K_H} = \frac{(1.25 \times 10^{-4} \text{ atm}) \times 760 \text{ torr}}{1.25 \times 10^6 \text{ torr}}$$

$$= 0.76 \times 10^{-7} = \frac{n_{CO_2}}{n \text{ Total}}$$

$$x_{H_2O} = (1 - 0.76 \times 10^{-7}) \approx 1 = \frac{n_{H_2O}}{n \text{ Total}}$$

$$\therefore \frac{n_{CO_2}/n \text{ total}}{n_{H_2O}/n \text{ total}} = \frac{n_{CO_2}}{n_{H_2O}} = \frac{0.76 \times 10^{-7}}{1} \approx 0.76 \times 10^{-7}$$

Molality of CO_2 solution

$$= \frac{x_{CO_2} \times 1000}{x_{H_2O} \times Mw_{H_2O}} = \frac{n_{CO_2} \times 1000}{n_{H_2O} \times Mw_{H_2O}}$$

$$= \frac{0.76 \times 10^{-7} \times 1000}{18}$$

$= 4.22 \times 10^{-6}$ m $\approx 4.22 \times 10^{-6}$ M.

$$H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{\ominus}$$

$$K = \frac{[H^{\oplus}][HCO_3^{\ominus}]}{[H_2CO_3]} \approx \frac{[H^{\oplus}]^2}{[H_2CO_3]}$$

$$\therefore [H^{\oplus}] = \sqrt{K_a [H_2CO_3]}$$

$$= \sqrt{4.3 \times 10^{-7} \times 4.22 \times 10^{-6}}$$

$$= \sqrt{1.814 \times 10^{-6}}$$

$$= 1.345 \times 10^{-6} \text{ M}$$

pH = 5.87

23. **(2)** 0.64 ppm = 0.64 g is 10^6 mL.

$$= \frac{0.64 \times 10^3 \text{ mL}}{64 \times 10^6 \text{ mL}} = 10^{-5} \text{ M } (Mw_{SO_2} = 64)$$

$[H^{\oplus}] = [SO_2] = 10^{-5}$ M

pH = 5.0

24. **(1)** $BaCl_2 + H_2SO_3 \longrightarrow BaSO_3 + 2HCl$

25. **(4)** Na_2SO_3 is a salt of W_A/S_B.

$pK_{a_2} = -\log(10^{-7}) = 7.$

(use pK_{a_2} value since SO_3^{2-} is used in salt formation)

$$\therefore pH = \frac{1}{2}(pK_w + pK_{a_2} + \log C)$$

$$= \frac{1}{2}(14 + 7 + \log 0.01) = \frac{1}{2}(21 - 2) = 9.5$$

26. **(2)** $K_a = \frac{K_{a_2}}{K_{a_1}} = \frac{10^{-7}}{10^{-2}} = 10^{-5}$

$$HSO_3^{\ominus}(aq) \rightleftharpoons SO_3^{2-} + H^{\oplus} \quad (K_{a_2})$$

$$HSO_3^{\ominus}(aq) + H^{\oplus} \rightleftharpoons SO_2(g) + H_2O(l) \quad \left(\frac{1}{K_{a_1}}\right)$$

$$2HSO_3^{\ominus}(aq) \rightleftharpoons SO_2(g) + SO_3^{2-}(aq) + H_2O(l)$$

27. **(1)** (Factual statement)

28. **(3)** pH of titration of strong acid with strong base is 7.

29. **(1)** Since the curve starts at higher pH (12.5), so it should be strong base and pH changes most rapidly near the equivalence point, so it should be strong acid. Hence the titration is strong base with strong acid (i.e., CsOH by HBr).

30. **(4)** Factual statement (refer section 8.16.2(b))

31. **(3)** Same explanation as in Q. 28 above.

32. **(1)** In Fig (1), there are two equivalence point and pH changes most rapidly at that point, so it is a titration of a weak diprotic acid by a strong base. At the end pH is very high and suggest a strong base.

Figs. (2), (3) and (4) do not have high, pH at the end. So strong base is not possible. Moreover pH does not change rapidly at equivalence point.

33. **(1)** According to Le Chatelier's principle, on adding O_2 at equilibrium, more of SO_2 will react with O_2 to give SO_3. So reaction shifts to the product side. Moreover volume of reaction vessel is reduced, i.e., pressure has increased, so the reaction shifts in the RHS, since there are less number of moles.

34. **(2)** Due to common ion (CrO_4^{2-}), the ionisation of Ag_2CrO_4 is suppressed and solubility of Ag_2CrO_4 decreases i.e., $[Ag^{\oplus}]$ decreases.

35. **(4)** S of AB $= \sqrt{K_{sp}} \qquad K_{sp} = S^2$

$$S \text{ of } A_2B = \sqrt[3]{\frac{K_{sp}}{4}} \qquad K_{sp} = 4S^3$$

$$S \text{ of } AB_3 = \sqrt[4]{\frac{K_{sp}}{27}} \qquad K_{sp} = 27S^4$$

Hence solubility of AB > A_2B > AB_3.

36. **(2)** If K_{a_1} is taken H_3PO_4 is a weak acid. (Mw H_3PO_4 = 98)

$$[H_3PO_4] = 0.05\% = \frac{0.05 \times 1000}{100 \times 98} = 5.1 \times 10^{-3} \text{ M}$$

$$pH_{WA} = \frac{1}{2}(pK_{a_1} - \log C)$$

$$= \frac{1}{2}(2.12 - \log 5.1 \times 10^{-3})$$

$$= \frac{1}{2}(2.12 - 0.7 + 3) = 2.21$$

37. **(3)** $K_{a_1} \times K_{a_2} \times K_{a_3} = \frac{[H^{\oplus}]^3 [PO_4^{3-}]}{[H_3PO_4]} \begin{bmatrix} [H_3PO_4] = 10^{-3} \\ pH = 7' \end{bmatrix}$

$$-\log K_{a_1} - \log K_{a_2} - \log K_{a_3} - \log [H_3PO_4]$$

$$= -3 \log [H^{\oplus}] - \log [PO_4^{3-}]$$

$$pK_{a_1} + pK_{a_2} + pK_{a_3} = 3pH - \log [PO_4^{3-}] + \log[H_3PO_4]$$

$$2.12 + 7.21 + 12.32 = 3 \times 7 - \log[PO_4^{3-}] - 3$$

$$\therefore \log [PO_4^{3-}] = -3.65$$

$$[PO_4^{3-}] = 2.24 \times 10^{-4}\ M$$

38. **(1)** $Zn_3(PO_4)_2 \rightleftharpoons 3Zn^{2+} + 2PO_4^{3-}$

$$K_{sp} = [Zn^{2+}]^3 [PO_4^{3-}]^2$$

$$9.1 \times 10^{-33} = (2.2 \times 10^{-4})^3 [PO_4^{3-}]^2$$

$$\therefore [PO_4^{3-}] = 2.9 \times 10^{-11}\ M$$

39. **(2) i.** Moles of $KMnO_4$ used $= \dfrac{6 \times 0.001}{1000} = 6 \times 10^{-6}$

$$\underset{2\text{ mol}}{2MnO_4^{\ominus}} + \underset{5\text{ mol}}{5C_2O_4^{2-}} + 16H^{\oplus} \longrightarrow$$

$$2Mn^{2+} + 10CO_2 + 8H_2O$$

ii. mol of $C_2O_4^{2-} = \dfrac{5}{2}$ mol of $MnO_4^{\ominus}$

$$= \frac{5}{2} \times 6 \times 10^{-6} = 1.5 \times 10^{-5}$$

40. **(1) i.** $5e^- + MnO_4^{\ominus} \longrightarrow Mn^{2+}$ ('n' factor = 5)

Equivalent of $MnO_4^{\ominus} = 5 \times$ mol. of $MnO_4^{\ominus}$

$$= 5 \times 6 \times 10^{-6} = 3 \times 10^{-5}$$

ii. $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ ('n' factor = 2)

Equivalent of $C_2O_4^{\ominus} = 2 \times 1.5 \times 10^{-5}$

$$= 3 \times 10^{-5}$$

41. **(3)** Moles of $C_2O_4^{2-} \longrightarrow 1.5 \times 10^{-5}\ (250\text{ mL})^{-1}$

$$[C_2O_4^{2-}] = [Ca^{2+}] = \frac{1.5 \times 10^{-5} \times 1000\text{ mL}}{250\text{ mL}} = 6 \times 10^{-5}\ M$$

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = (6 \times 10^{-5})^2 = 3.6 \times 10^{-9}\ M^2$$

42. **(3)** $KMnO_4$ is a self indicator and imparts its own colour.

43. **(1) i.**

$$\begin{array}{llll} & H_3PO_4 & \xrightleftharpoons{K_1 = 10^{-3}} H^{\oplus} & + \ H_2PO_4^{\ominus} \\ \text{Initial} & C & 0 & 0 \\ \text{At equilibrium} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$1 \times 10^{-3} = \frac{C\alpha^2}{1-\alpha} = \frac{0.05 \times \alpha^2}{1-\alpha}$$

(Neglecting α wrt 1)

Using direct formula for pH of weak acid ($pK_{a1} = 3$, $C = 0.05$)

$$pH = \frac{1}{2}(pK_{a_1} - \log C) = \frac{1}{2}(3 - \log 0.05)$$

$$= \frac{1}{2}(3 - 0.7 + 2) = 2.15$$

ii. For an acidic indicator:

$$HIn \xrightleftharpoons{K_{Ind}} H^{\oplus} + Ind^{\ominus}.$$

$$\therefore pH = pK_{Ind} + \log \frac{[Ind^{\ominus}]}{[HIn]}$$

$$2.15 = 7 + \log \frac{[Ind^{\ominus}]}{[HIn]} \quad (K_{Ind} = 10^{-7})$$

$$\log \frac{[Ind^{\ominus}]}{[HIn]} = 2.15 - 7 = -4.85$$

$$\frac{[Ind^{\ominus}]}{[HIn]} = \text{Antilog}\ (-4.85)$$

$$= \text{Antilog}\ (-4 - 0.85 + 1 - 1)$$

$$= \text{Antilog}\ (\bar{5}.15) = 1.413 \times 10^{-5}$$

44. **(1)** When colour P predominates over Q, then,

$$pH = pK_{Ind} + \log 120$$

$$pH = 7 + \log 120 = 9.0792$$

When colour Q predominates over P, then

$$pH = pK_{Ind} + \log \frac{1}{127}$$

$$pH = 7 - \log 127 = 4.896$$

pH range of indicator is 4.896 to 9.0792

45. **(1)** At 1st neutralisation point, H_3PO_4 is converted to KH_2PO_4, here pH of the solution

$$\frac{pK_1 + pK_2}{2} = \frac{3+7}{2} = 5$$

At 2nd neutralisation point, H_3PO_4 is converted to KH_2PO_4,

$$\therefore\ pH = \frac{pK_2 + pK_3}{2} = \frac{7+13}{2} = 10$$

The equivalence point will be obtained when acid H_3PO_4 will change into K_2HPO_4.

('n' factor for acid = 2) ($2H^{\oplus}$ ions are replaced)

mEq of H_3PO_4 = mEq of NaOH

$$0.05 \times 30 \times 2 = 30 \times M$$

$$M_{NaOH} = 0.1\ M$$

Matrix Match Type

1. **(a → q)** Salt of W_A/S_B, $pH = \dfrac{1}{2}(pK_w + pK_a + \log C)$

$$= \frac{1}{2}(14 + pK_a + \log 10^{-1})$$

$$= 6.5 + \frac{1}{2} pK_a$$

(b → r) Salt of W_B/S_A, $pH = \dfrac{1}{2}(pK_w - pK_a - \log C)$

$$= \frac{1}{2}(14 - pK_b - \log 10^{-1})$$

$$= 7.5 - \frac{1}{2} pK_b$$

(c → p) Salt of S_A/S_B, (do not hydrolyse), pH = 7

(d → p, s) salt of W_A/W_B,

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

$$= 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b = 7 \text{ since } (pK_a = pK_b)$$

2. (a → p) Acidic buffer (mixture of W_A + salt of W_A/S_B)

$$\text{pH} = \text{p}K_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$$

$$= 4.74 + \log\left(\frac{0.1}{0.1}\right) = 4.74$$

Thus, it is acidic buffer at maximum buffer capacity. Because buffer limits are pH ± 1. When $\text{pH} = \text{p}K_a$, it is a buffer at maximum buffer capacity.

(b → r) It is mixture of W_A and S_A. So pH of 0.1 M HCl will predominate and $\text{pH} < 7$.

(c → s) It will forms salt of W_A/W_B. Since $\text{p}K_a = \text{p}K_b$,

Thus pH = 7. $\left(\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \text{p}K_b)\right)$

(d → q) mmol of $CH_3COONa = 300 \times 0.1 = 30$

mmol of HCl = HCl = $100 \times 0.1 = 10$.

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$$

Inital	30 mmol	10 mmol	0	0
Final	(30–10)=20	(10–10)=0	10	—

It is a mixture of W_A and salt of W_A/S_B. It forms acidic buffer.

$$\text{pH} = \text{p}K_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$$

(Total volume = 300 + 100 = 400 mL)

$$= 4.74 + \log\left[\frac{20/400}{10/400}\right]$$

$$= 4.74 + 0.3 = 5.03$$

3. (a → q; b → p; c → s; d → r; e → t)

(Refer Table 8.11 and section 8.23)

4. (a → p) Acidic salt: aqueous solution of salt is acidic

$(\text{pH} < 7)$ $\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log C)$

(b → q) Basic salt: Aqueous solution of salt is basic

$(\text{pH} > 7)$ $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_b + \log C)$

(c → s) Acidic buffer: $\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

(d → r) Basic buffer: $\text{pOH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$

5. (a → q) NH_4Cl: only $\overset{\oplus}{N}H_4$ will get hydrolysed.

(b → r) CH_3COONa: only $CH_3COO^{\ominus}$ will get hydrolysed.

(c → s) NH_4CN: Both $\overset{\oplus}{N}H_4$ and $CN^{\ominus}$ will get hydrolysed.

(d → p) NaCl: Neither $Na^{\oplus}$ nor $Cl^{\ominus}$ will get hydrolysed.

6. (a → p, t) Only $\overset{\oplus}{N}H_4$ will get hydrolysed (cation hydrolysis) $\text{pH} < 7$.

$$\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log C)$$

(b → s, t) It is a S_A. pH = 2, New conc $= \frac{10^{-2}}{10} = 10^{-3}$, pH = 3

(c → r) It is a W_B, so $\text{pH} > 7$.

(d → p, q) Salt of W_A/W_B both $CH_3COO^{\ominus}$ and $\overset{\oplus}{N}H_4$ will hydrolysed so both cationic and anionic hydrolysis.

7. (a → q) S in buffer $= \left[K_{sp}\left(1 + \frac{H^{\oplus}}{K_a}\right)\right]^{1/2}$

S in $H_2O = \sqrt{K_{sp}}$

$$\frac{S \text{ in buffer}}{S \text{ in } H_2O} = \frac{\sqrt{K_{sp}}\left(1 + \frac{H^{\oplus}}{K_a}\right)^{1/2}}{\sqrt{K_{sp}}} = \left(1 + \frac{10^{-3}}{10^{-3}/3}\right)^{1/2} = 2$$

(b → p) $\frac{S \text{ in buffer}}{S \text{ in } H_2O}$

$$= \left(1 + \frac{H^{\oplus}}{K_a}\right)^{1/2} = \left(1 + \frac{10^{-4}}{10^{-4}/7}\right)^{1/2} = 4$$

(c → s) $\frac{\text{S in buffer}}{\text{S in } H_2O}$

$$= \left(1 + \frac{H^{\oplus}}{K_a}\right)^{1/2} = \left(1 + \frac{10^{-5}}{10^{-5}/8}\right)^{1/2} = 3$$

(d → q) S in 0.1 M HCl $= \frac{K_{sp}}{0.1}$

S in 0.2 M $AgNO_3 = \frac{K_{sp}}{0.2}$

$$\frac{\text{S in HCl}}{\text{S in } AgNO_3} = \frac{K_{sp} \times 0.2}{0.1 \times K_{sp}} = 2$$

(e → r) S in 0.1 M HCl $= \frac{K_{sp}}{(0.1)^3}$

S in 0.2 M NaOH $= \frac{K_{sp}}{(0.2)^3}$

$$\frac{\text{S in 0.1 MHCl}}{\text{S in 0.2 M NaOH}} = \frac{K_{sp} \times (0.2)^3}{(0.1)^3 \times K_{sp}} = 8$$

8.

	V_{NaOH} mL	V_{total} mL in excess	mmol of CH_3COOH $(CH_3COO^{\ominus})$ produced	mmol of salt excess	mmol of $\overset{\ominus}{O}H$ in	Type
a.	25.0	25+50=75	2.5	2.5	—	Acidic buffer
b.	40.0	40+50 =90	1.0	4.0	—	Acidic buffer

c.	50.0	50+50 =100	0.00	5.0	—	Salt of W_A/S_B
d.	60.0	60+50=110	—	5.0	1.0	S_B
e.	70.0	70+50=120	—	5.0	2.0	S_B

(a → r) $\mathrm{pH} = \mathrm{p}K_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$= 4.74 + \log\left(\frac{2.5/75}{2.5/75}\right) = 4.74$$

(b → q) $\mathrm{pH} = \mathrm{p}K_a + \log\left(\dfrac{4.0/90}{1.0/90}\right) = 4.74 + 0.6 = 5.34$

(c → t) $\mathrm{pH} = \dfrac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a + \log C)$

$$= \frac{1}{2}(14 + 4.74 + \log 5/100) = 8.72$$

(d → q) $[\overset{\ominus}{O}H] = \dfrac{1.0 \text{ mmol}}{110 \text{ mL}} = 9.1 \times 10^{-3}$ M

pOH = 2.04, pH = 11.96

(e → s) $[\overset{\ominus}{O}H] = \dfrac{2.0 \text{ mmol}}{120 \text{ mL}} = 1.7 \times 10^{-2}$ M.

pOH = 1.78. pH = 12.22

9.

	V_{NaOH} mL excess	mmol H_2S in produced	mmol $HS^{\ominus}$ produced	mmol S^{2-}	pH
a.	0.001	1.00	0.00	–	4.5
b.	0.5	0.5	0.5	–	7.0
c.	1.0	0.0	1.0	0.0	9.5 and 12.0
d.	1.5	–	0.5	0.5	11.7

$$H_2S + H_2O \longrightarrow HS^{\ominus} + H_2O;$$

$$\Rightarrow K_1 = \frac{[H_3O^{\oplus}][HS^{\ominus}]}{[H_2S]} = 10^{-7}$$

$$HS^{\ominus} + H_2O \longrightarrow H_3O^{\oplus} + S^{2-}$$

$$\Rightarrow K_2 = \frac{[H_3O^{\oplus}][S^{2-}]}{[HS^{\ominus}]} = 10^{-14}$$

The total volume of the titration mixture will change only slightly. Titrations (a) and (b) is calculated directly from the K_1 value of H_2S.

(a → q) $\dfrac{x \times x}{0.01} = 10^{-7}$ so $x = [H_3O^{\oplus}] = 3.1 \times 10^{-5}$ and pH $= 4.5$

(b → p) $\dfrac{x(0.5)}{0.5} = 10^{-7}$, so pH = 7.0

(c → r, t)

i. Point (c) is the first equivalence point the same solution as 1.0 mol of NaHS in 101.0 mL. The $HS^{\ominus}$ can react in water to ionise is either of the two ways:

$$HS^{\ominus} + H_2O \longrightarrow H_3O^{\oplus} + S^{2-} \; (K_2 = 10^{-14}) \quad \text{...(i)}$$

$$HS^{\ominus} + H_2O \longrightarrow \overset{\ominus}{O}H + H_2S \quad \text{...(ii)}$$

$$K_h = \frac{K_w}{K_1} = \frac{10^{-14}}{10^{-7}} = 10^{-7}$$

Equation (ii) will predominate, therefore ignore equation (i).

Hence, this case becomes the hydrolysis of salt of W_A/S_B. Considering K_1 of H_2S. (pK_a H_2S =7).

$$\therefore \; \mathrm{pH} = \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_1 + \log C)$$

$$= \frac{1}{2}\left(14 + 7 + \log\frac{1}{101}\right)$$

$$= \frac{1}{2}(14 + 7 + \log 10^{-2})$$

$$= \frac{1}{2}(14 + 7 - 2) = 9.5$$

ii. With $HS^{\ominus}$ hydrolysing much more than ionising to yield $H_3O^{\oplus}$, it might be well to calculate the hydrolysis of S^{2-} at the second equivalence point.

$$S^{2-} + H_2O \longrightarrow HS^{\ominus} + \overset{\ominus}{O}H,\; K_h = \frac{K_w}{K_2} = \frac{10^{-14}}{10^{-14}} = 1$$

$$\therefore \quad \frac{x^2}{0.01 - x} = 1 \text{ or } x^2 + x - 0.01 = 0$$

$$\frac{-1 + \sqrt{1 + 0.04}}{2} = 1 \times 10^{-2} \quad [\overset{\ominus}{O}H] \text{ thus pOH} = 2.$$

pH = 12.0

The extra $\overset{\ominus}{O}H$ ions added after the first equivalence point have not been neutralised by the very weak $HS^{\ominus}$ ion, i.e., titration is some what like that of weak acid (CH_3COOH).

(d → s) When 1.5 mL of NaOH added: (Total volume = 100 + 1.5 = 101.5 ≈ 100 mL)

$$[S^{2-}]_{\text{initial}} = \frac{0.5}{100} = 0.5 \times 10^{-2} \text{ or } 5 \times 10^{-3}$$

$$[HS^{\ominus}]_{\text{initial}} = \frac{0.5}{100} = 0.5 \times 10^{-3}$$

	S^{2-} +	$H_2O \longrightarrow$	$HS^{\ominus}$ +	$\overset{\ominus}{O}H$
Initial	5×10^{-3}	–	5×10^{-3}	0
At equilibrium	$(5 \times 10^{-3} - x)$	–	$(5 \times 10^{-3} + x)$	x

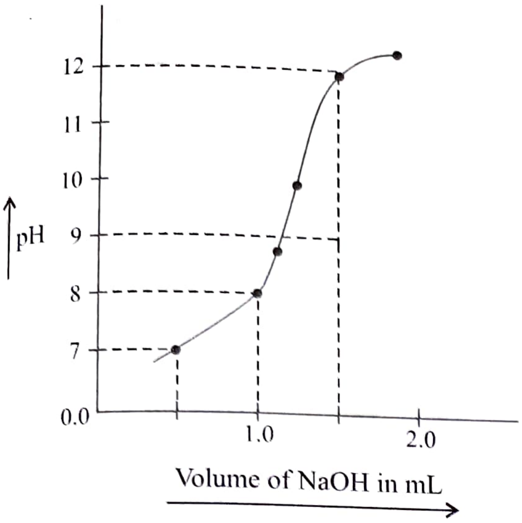
$$K_h = \frac{K_w}{K_2} = \frac{10^{-14}}{10^{-14}} = 1$$

$$\therefore K_h = \frac{[HS^{\ominus}][\overset{\ominus}{O}H]}{[S^{2-}]}$$

$$1 = \frac{(5 \times 10^{-3} + x)\,x}{(5 \times 10^{-3} - x)}. \text{ Thus } x = 5 \times 10^{-3} = [\overset{\ominus}{O}H]$$

pOH = 2.3 and pH = 11.7

Graphical representation



0. **(a → q)** Basic buffer is formed.

mmol of HCl added = 2.0 × 1L = 2.

mmol of $\overset{\oplus}{N}H_4$ formed = 2.

mmol of NH_3 left

$(1 \times 0.01 \times 10^3 = 10) = 10 - 2 = 8$

$$pOH = pK_b + \log\frac{[\overset{\oplus}{N}H_4]}{[NH_3]}$$

$$= 4.74 + \log\frac{2}{8} = 4.14$$

(b → r) $\left[\frac{\overset{\oplus}{N}H_4}{NH_3}\right] = \left(\frac{5}{5}\right) = 1.0$

$pOH = 4.74.$

(c → s) In (c) salt of W_B/S_A is formed.

$(V_{total} = 1\ L + 5\ mL \approx 1\ L)$

$$[NH_4Cl] = \frac{0.01}{1.01\ L} \approx 0.01\ M$$

$$pH = \frac{1}{2}(pK_w - pK_b - \log C)$$

$$= \frac{1}{2}(14 - 4.74 - \log 10^{-2}) = 5.63$$

$pOH = 14 - 5.63 = 8.37$

(d → p) When 11.0 mL of HCl is added, all the NH_3 is neutralised and 1.0 mmol of HCl is in excess. pH is determined by 1.0 mmol of $H_3O^{\oplus}$ in 1.01 L.

$$[H_3O^{\oplus}] = \frac{1 \times 10^{-3}\ mol}{1.01 L} \approx 10^{-3},$$

pH = 3, and pOH = 11.

(a → r, s) $HSO_4^{\ominus} + H_2O \longrightarrow H_3O^{\oplus} + SO_4^{2-}$
(Bronsted acid)

$HSO_4^{\ominus} + H^{\oplus} \longrightarrow H_2SO_4$ (Bronsted base)

(b → p) BF_3 (e^- deficient and hence Lewis acid).

(c → q, s) H_3N: (It can donate lone pair of electrons and acts as Lewis base)

$NH_3 + H_2O \longrightarrow \overset{\oplus}{N}H_4 + \overset{\ominus}{O}H$ (Accepts $H^{\oplus}$ and acts as Bronsted base)

(d → q, s) $\overset{\ominus}{O}H$ (It is bronsted base by accepting $H^{\oplus}$) It can donate lone pair of electrons and acts as Lewis base also.

12. (a → p, s; b → r; c → q; d → p, q, s)

Refer Table 8.9.

13. (a → p; b. → q; c → r ; d → s)

All factual statements.

14. (a → q) $Li_3Na_3(AlF_6)_2 \rightleftharpoons 3Li^{\oplus} + 3Na^{\oplus} + 2(AlF_6)^{-3}$

$\qquad 3x \qquad 3x \qquad 3x$

$$K_{sp} = 3^3\,3^3\,2^2\,x^8 = 2916\,x^8$$

(b → t) $Zr_3(PO_4)_4 \rightleftharpoons 3Zr^{+4} + 4PO_4^{3-}$

$\qquad 3x \qquad 4x$

$$K_{sp} = 3^3 4^4 x^7 = 6912x^7$$

(c → p) $Bi_2S_3 \rightleftharpoons 2Bi^{3+} + 3S^{2-}$

$\qquad 2x \qquad 3x$

$$K_{sp} = 2^2 3^3 x^5 = 108x^5$$

(d → r) $Al(OH)_3 \rightleftharpoons Al^{3+} + 3\overset{\ominus}{O}H$

$\qquad x \qquad 3x$

$$K_{sp} = 1^1 3^3 x^4 = 27x^4$$

(e → s) $CaF_2 \rightleftharpoons Ca^{3+} + 2F^-$

$\qquad x \qquad 3x$

$$K_{sp} = 1^2 2^3 x^3 = 4x^3$$

Numerical Value Type

1. (54)

1. I. HCN is W_A; $pH_{W_A} = \frac{1}{2}(pK_a - \log C)$

$$= \frac{1}{2}(10 - \log 10^{-1}) = 5.5$$

II. Acidic buffer: $pH_{acidic\ Buffer} = pK_a + \log\frac{0.1}{0.1} = 5$

III. HCl is S_A: pH = – log (0.1) = 1

IV. NH_4OH is W_B: $pOH_{W_B} = \frac{1}{2}(pK_a - \log C)$

$$= \frac{1}{2}(5 + 1) = 3$$

pH = 14 – 3 = 11

V. NaOH is S_B: pOH = – log (0.01) = 2,

pH = 14 – 2 = 12

VI. Salt of W_A/W_B: pH = 7

∴ Magic number = 5.5 × 2 + 5 × 1 + 1 × 3 + 11 × 2 + 12 × 0.5 + 7 × 1 = 54

2. (4)

II A group: Pb^{2+}, Cu^{2+}.

III group: Cr^{3+},

IV group: Zn^{2+}.

(b), (d), (e), and (f).

All salts (b, d, and f), soluble hydroxides and the acid (e) are strong electrolytes.

4. (5)

Acidic

$$\left[\text{HClO}_4, \text{HCl}, \text{HC}_2\text{H}_3\text{O}_2, \frac{(\text{NH}_4)_2\text{SO}_4 \text{ and NH}_4\text{Cl}}{\text{Both salt of W}_\text{B}/\text{S}_\text{A}}\right]$$

(Five compounds)

5. (2)

Neutral [NaCl and K_2SO_4] Both salts of S_A/S_B.

6. (3)

Basic [$NH_3 + NH_4Cl$ (basic buffer), NH_3, NaOH]

The basic buffer is less basic than NH_3 alone because the $\overset{\oplus}{NH_4}$ suppresses the ionisation of NH_3 in the buffer.

7. (3, 2, 1, 1)

a. (3)

Salt of W_A/W_B and W_B/S_A hydrolyses more in water.

iii. $NaC_2H_3O_2$ (salt of W_A/S_B) $\longrightarrow C_2H_3O_2^{\ominus}$.

iv. NH_4Cl (salt of W_B/S_A) $\longrightarrow \overset{\oplus}{NH_4}$

v. MgS (salt of W_A/S_B) $\longrightarrow S^{2-}$

b. (2)

Salt of S_A/S_B do not hydrolyse.

vi. Na_2SO_4 **viii.** KCl

c. (1)

Salt of W_A/S_B ($NH_4C_2H_3O_2$) with same value of K_a and K_b, both hydrolyse to the same extent. (K_a of CH_3COOH $= K_b$ of NH_3)

d. (1)

ii. Salt of W_A/W_B with different K_a and K_b, both hydrolyse to the same extent. ($PhCOONH_4$ have different K_a and K_b)

8. (6)

(a), (b), (g), (h) and (k)

a. $\underset{W_A}{CH_3COOH} + H_2O \longrightarrow H_3O^{\oplus} + CH_3COO^{\ominus}$ (< 2%)

b. $\underset{\text{Salt of } W_A}{CH_3COO^{\ominus}} + H_2O \longrightarrow CH_3COOH + \overset{\ominus}{O}H$ (< 2%)

g. $Cl^{\ominus} + H_3O^{\oplus} \longrightarrow$ No reaction

h. $Cl^{\ominus} + H_2O \longrightarrow$ No reaction

k. $NH_3 + H_2O \longrightarrow \overset{\oplus}{NH_4} + \overset{\ominus}{O}H$

n. $K^{\oplus} + \overset{\ominus}{O}H \longrightarrow$ No reaction.

9. (8)

c. $CH_3COO^{\ominus} + H_3O^{\oplus} \longrightarrow CH_3COOH + H_2O$ (> 98%)

d. $CH_3COOH + \overset{\ominus}{O}H \longrightarrow CH_3COO^{\ominus} + H_2O$ (> 98%)

e. $CH_3COO^{\ominus} + H_3O^{\oplus} \longrightarrow CH_3COOH + H_2O$ (> 98%)

f. $HCl + H_2O \longrightarrow H_3O^{\oplus} + Cl^{\ominus}$ (> 98%)

i. $\overset{\oplus}{NH_4} + \overset{\ominus}{O}H \longrightarrow NH_3 + H_2O$ (> 98%)

j. $\overset{\oplus}{NH_4} + \overset{\ominus}{O}H \longrightarrow NH_3 + H_2O$ (> 98%)

l. $NH_3 + H_3O^{\oplus} \longrightarrow \overset{\oplus}{NH_4} + H_2O$ (> 98%)

m. $NH_3 + H_3O^{\oplus} \longrightarrow \overset{\oplus}{NH_4} + H_2O$ (> 98%)

10. (7)

Salt of W_A/S_B (CH_3COONa) is formed.

If we calculate pH by using hydrolysis formula for salt of W_A/S_B.

$$\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C) \quad \Bigg]\text{Salts of } S_A$$

$$\left[[\text{Salt}] = \frac{10^{-6}}{2}\left(\begin{matrix}\text{Volume is}\\ \text{doubled}\end{matrix}\right)\right]$$

$$= \frac{1}{2}\left(14 + 4.7 + \log\frac{10^{-6}}{2}\right)$$

$$= \frac{1}{2}(18.7 - 6 - 0.3) = 6.2$$

But pH of salt of W_A/S_B is always > 7.

So for such dilute solutions of CH_3COOH and NaOH.

Contribution of $\overset{\ominus}{O}H$ ions from H_2O must be considered.

$$\begin{matrix} CH_3COOH & + & NaOH & \longrightarrow & CH_3COONa & + & H_2O \\ 10^{-6}\text{ M} \times V & & 10^{-6}\text{ M} \times V & & 10^{-6}\text{ M} \times V & & \end{matrix}$$

$$[CH_3COONa] = \frac{10^{-6}\text{ M} \times V}{2V} = 0.5 \times 10^{-6}$$

$$= 5 \times 10^{-7} < 10^{-6}\text{ M}$$

$$[\overset{\ominus}{O}H] = \left(\frac{K_w \times C}{K_a}\right)^{1/2} = \left(\frac{10^{-14} \times 5 \times 10^{-7}}{2 \times 10^{-5}}\right)^{\frac{1}{2}}$$

$$= (2.5)^{\frac{1}{2}} \times 10^{-8}\text{ M} = 1.58 \times 10^{-8}\text{ M} < 10^{-6}\text{ M}$$

$$\text{Total } [\overset{\ominus}{O}H] = [1.58 \times 10^{-8} + 10^{-7} \text{ (from } H_2O)]$$

$$= 10^{-7}(1.58 \times 10^{-1} + 1) = 1.158 \times 10^{-7}$$

$$\text{pOH} = -\log(1.158 \times 10^{-7}) = 6.93$$

$$\text{pH} = 14 - 6.93 = 7.07 \approx 7.$$

Archives

JEE Main

Single Correct Answer Type

1. (1)

pH of a solution = 5

∴ $[H^+] = 10^{-\text{pH}} = 10^{-5}$

HA (a weak acid) ionizes as

$HA \rightleftharpoons H^+ + A^-$

$$\begin{array}{lll} 1.0 & 0 & 0 \\ (1-10^{-5}) & 10^{-5} & 10^{-5} \end{array}$$

$$K_a \frac{[H^-][A^-]}{[HA]} = \frac{10^{-5} \times 10^{-5}}{(1-10^{-5})} = \frac{10^{-10}}{1} \quad [1 >>> 10^{-5}]$$

$$= 1 \times 10^{-10}\text{ M}$$

2. (1)

Only in reaction (II), $H_2PO_4^-$ gives H^+ to H_2O. Thus, behaves as an acid.

3. (3)

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.2 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 4.8 \times 10^{-11}$

$K_1 >> K_2$

$\therefore$ $[H^+] = [HCO_3^-]$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

So. $[CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

4. (2)

$[AgBr] = [Ag^+] = 0.05$ M

$K_{sp}[AgBr] = [Ag^+]\,[Br^-]$

$$\Rightarrow \quad [Br^-] = \frac{K_{sp}(AgBr)}{[Ag^+]}$$

$$= \frac{5.0 \times 10^{-13}}{0.05} = 10^{-11}\text{M}\,[\text{mol L}^{-1}]$$

Moles of KBr needed to precipitate AgBr

$= [Br^-] \times V = 10^{-11}$ mol $L^{-1} \times 1$ L $= 10^{-11}$ mol

Therefore, amount of KBr needed to precipitate AgBr

$= 10^{-11}$ mol $\times$ 120 g $mol^{-1} = 1.2 \times 10^{-9}$ g

5. (2)

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$K_{sp} = [Mg^{2+}]\,[OH^-]^2$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1 \times 10^{-11}}{0.001}} = 10^{-4}$$

pOH $= -\log [OH^-] = -\log [10^{-4}] = 4$

$\therefore$ pH $= 14 - $ pOH $= 14 - 4 = 10$

6. (2)

$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$

$[Na_2CO_3] = [CO_3^{2-}] = 1 \times 10^{-4}$ M

$BaCO_3 \rightleftharpoons Ba^{2+} + CO_3^{2-}$

$$K_{sp(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$$

$$[Ba^{2+}] = \frac{K_{sp}(BaCO_3)}{[CO_3^{2-}]}$$

$$[Ba^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}} = 5.1 \times 10^{-5}\text{ M}$$

Hence, at 5.1×10^{-5} concentration of Ba^{2+}, a precipitate will begin to form.

7. (2) For the hydrolysis of a salt of weak acid and weak base

$$pH = 7 + \frac{1}{2}[pK_a - pK_b]$$

$$pH = 7 + \frac{1}{2}[3.2 - 3.4] = 6.9$$

8. (1) Salt of strong base and weak acid results in basic solution on hydrolysis.

(1) $\underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong base}}{KOH} \longrightarrow CH_3COOK + H_2O$

(2) $\underset{\text{Weak base}}{Fe(OH)_3} + \underset{\text{Strong acid}}{HCl} \longrightarrow FeCl_3 + H_2O$

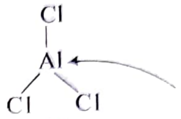
Its hydrolysis will produce acidic solution

(3) $\underset{\text{Weak acid}}{Pb(OH)_2} + \underset{\text{Weak base}}{CH_3COOH} \longrightarrow (CH_3COO)_2Pb + H_2O$

(4) $\underset{\text{Weak base}}{Al(OH)_3} + \underset{\text{Weak acid}}{HCN} \longrightarrow Al(CN)_3 + H_2O$

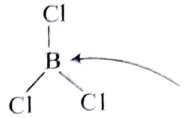
9. (3) L.A. are those which can accept pair of electrons

$AlCl_3$



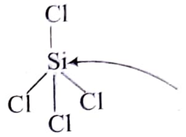
Six electrons around aluminium make it lewis acid

BCl_3



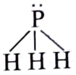
Six electrons around boron make it lewis acid

$SiCl_4$



Si can expand its covalency due to availability of d-orbitals but due to its small size it can't be surrounded by six chloride ion.

PH_3



Not a lewis acid

10. (2) $Ba^{+2} + \rightleftharpoons BaSO_{4(s)}$

ppt

$$\text{Final conc. of }[SO_4^{2-}] = \frac{MV_1}{V_1 + V_2} = \frac{1 \times 50}{500} = 0.1\text{ M}$$

Final conc. of $[Ba^{2+}]$ when $BaSO_4$ start precipitating

$K_{SP} = Q_{SP} = [Ba^{+2}][SO_4^{2-}]$

$10^{-10} = [Ba^{+2}](0.1M)$

$[Ba^{+2}] = 10^{-9}$ M

initial conc. $[Ba^{+2}]$; initial volume was = 500 – 50 = 450 ml

$M_1V_1 = M_2V_2$

$$M_1 = \frac{M_2V_2}{V_1} = \frac{10^{-9} \times 500}{450}$$

$M_1 = 1.1 \times 10^{-9}$ M

JEE Advanced

Single Correct Answer Type

1. **(1)** In acidic solution $[S^{2-}]$ is low. So CuS and HgS (II group cations) will be precipitated more easily due to low K_{sp} value.

   NiS and MnS (IV group cation) will precipitate if H_2S is passed in basic medium.

2. **(3)** Initial pH = 1, i.e. $[H^{\oplus}] = 0.1$ mole/litre

   New pH = 2, i.e. $[H^{\oplus}] = 0.01$ mole/litre

   In case of dilution : $M_1V_1 = M_2V_2$

   $0.1 \times 1 = 0.01 \times V_2$

   $V_2 = 10$ litre

Volume of water added = (10 – 1) = 9L

3. (2) $K_{sp} = 1.1 \times 10^{-12} = [Ag^{\oplus}]^2 [CrO_4^{2-}]$

$1.1 \times 10^{-12} = [0.1]^2 [S]$

$S = 1.1 \times 10^{-10}$

4. (1) Rate in weak acid = $\frac{1}{100}$ (rate in strong acid)

$\therefore \quad [H^{\oplus}]_{\text{weak acid}} = \frac{1}{100} = [H^{\oplus}]_{\text{strong acid}}$

$\therefore \quad [H^{\oplus}]_{\text{weak acid}} = \frac{1}{100} M = 10^{-2}\,M$

$\therefore \quad C\alpha = 10^{-2} = 1 \times \alpha = 10^{-2}$

$\therefore \quad \alpha = 10^{-2}$

$K_a = C\alpha^2 \qquad (C = 1M)$

$= 1 \times (10^{-2})^2$

$K_a = 10^{-4}$

Option (1) is correct.

Multiple Correct Answers Type

1. (3, 4)

(1) Not buffer since it is a mixture of S_A and W_A.

(2) Not buffer since it is a mixture of S_B and salt of W_A/S_B.

(3) It is an acidic buffer. Since some of HNO_3 will react with CH_3COONa to produce weak acid and some CH_3COONa to produce weak acid and some CH_3COONa will be left. So buffer is formed.

	HNO_3 +	$CH_3COONa \longrightarrow$	$NaNO_3$ +	CH_3COOH
Initial	x	y	0	0
Final	—	$(y-x)$	$(y-x)$	$(y-x)$

(4) It is an acidic buffer (mixture of W_A and salt of W_A/S_B)

Matrix Match Type

1. (4)

$$\frac{K_w}{K_a} = \frac{[CH_3COO^-][OH^-]}{[CH_3COOH]}$$

$$[OH-] = \left(\frac{K_w}{K_a} \times C\right)^{1/2}$$

(P) is a buffer, so $[H^+]$ does not change on dilution, as [salt] = [acid].

(Q) contains only CH_3COONa

So, $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$[OH^-] = \sqrt{K_h \times C} \Rightarrow [H^+]$ decreases by $\sqrt{2}$ times

(R) is also salt hydrolysis

So, $NH^+_4 + H_2O \rightleftharpoons NH_4OH + H^+$

$$[H^+] = \sqrt{\frac{K_w}{K_b} \times C}$$

So, C is made $\frac{1}{2}$ so, $[H^+]$ becomes $\frac{1}{\sqrt{2}}$

(S) it is a solubility equilibria

So dilution does not effect $[H^+]$ or $[OH^-]$

Numerical Value Type

1. (8) For a salt of weak acid and strong base,

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$
$$= 7 + \frac{1}{2}(-\log \times 10^{-4}) + \frac{1}{2} \log 0.01 = 8$$

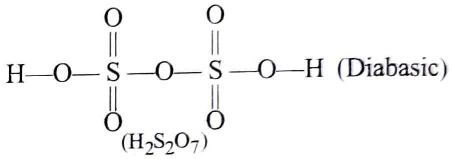
2. (3) Salts of strong bases and weak acids turn red litmus to blue.

KCN, H_3PO_3, LiCN

3. (6) Diprotic acids are those which furnish two protons per molecule.

H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_3CrO_4, H_2SO_3

$H_3BO_3 + H_2O \longrightarrow B(OH)_4^{\ominus} + H^{\oplus}$ (Monobasic)



$H{-}O{-}S(=O)_2{-}O{-}S(=O)_2{-}O{-}H$ (Diabasic)

$(H_2S_2O_7)$

Only those hydrogens are replaceable from oxy-acids of phosphorous and sulphur which are attached to oxygen.

H_3PO_4 (Tribasic)
H_3PO_3 (Dibasic)
H_3PO_2 (Monobasic)

4. (7)

$$AgCl \rightleftharpoons \underset{S'}{Ag^{\oplus}} + \underset{(S'+x)}{Cl^{\ominus}} \quad (K_{sp} = 1.6 \times 10^{-10})$$

$$CuCl \rightleftharpoons \underset{x}{Cu^{\oplus}} + \underset{(x+S')}{Cl^{\ominus}} \quad (K_{sp} = 1 \times 10^{-6})$$

$\therefore S'(S' + x) = 1.6 \times 10^{-10}$

$x(x + S') = 10^{-6}$

$\frac{S'}{x} = 1.6 \times 10^{-4}$

$\therefore S' = (1.6 \times 10^{-4})x \Rightarrow x(x + 1.6 \times 10^{-4}x) = 10^{-6}$

$\Rightarrow x = 10^{-3}$

$\therefore S' = 1.6 \times 10^{-7} = 1.6 \times 10^{-x}$ (The value of $x = 7$)

Alternative method:

$Cl^{\ominus}$ will be from CuCl (Since CuCl is more soluble than AgCl as it is evident from their K_{sp} value)

$K_{sp} = [Cu^{\oplus}][Cl^{\ominus}] = 10^{-6} = x \times x \Rightarrow x = 10^{-3}$

Since AgCl is sparingly soluble.

K_{sp} of AgCl = $[Ag^{\oplus}](10^{-3})$

$1.6 \times 10^{-10} = [Ag^{\oplus}](10^{-3})$

$\therefore [Ag^{\oplus}] = 1.6 \times 10^{-7} = 1.6 \times 10^{-x}$ (the value of $x = 7$)

5. (4.47)

$$AB \rightleftharpoons \underset{s}{A^+} + \underset{(s-x)}{B^-}$$

$$2 \times 10^{-10} = S(S - x) \quad \text{...(1)}$$

$$\underset{(S-x)}{B^-} + \underset{10^{-3}}{H^+} \rightleftharpoons \underset{x}{HB}$$

$$\frac{1}{10^{-8}} = \frac{x}{(S-x)\times 10^{-3}}$$

$$\frac{x}{S-x} = 10^5 \quad \text{...(2)}$$

Multiply equation (1) and (2).

$S.x = 2 \times 10^{-5}$

From Eq. (1)

$S^2 - Sx = 2 \times 10^{-10}$

$S^2 - 2 \times 10^{-5} = 2 \times 10^{-10}$

$S^2 = 2 \times 10^{-5} + 2 \times 10^{-10} \cong 2 \times 10^{-5}$

$S = 4.47 \times 10^{-3}$

$y = 4.47$

2

APPENDIX

Chapterwise Solved January 2019 JEE Main Questions (All Sets)

Chapter 1
Some Basic Concepts and Mole Concept

1. A solution of sodium sulfate contains 92 g of $Na^{\oplus}$ ions per kilogram of water. The molality of $Na^{\oplus}$ ions in that solution in mol kg^{-1} is:
(1) 16 (2) 8
(3) 4 (4) 12

2. For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is:
$2C_{57}H_{110}O_6(s) + 163\ O_2(g) \rightarrow 114\ CO_2(g) + 110\ H_2O(l)$
(1) 495 g (2) 490 g
(3) 890 g (4) 445 g

3. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is:
(1) 68.4 g (2) 17.1 g
(3) 34.2 g (4) 136.8 g

4. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 ml of CO_2 at $T = 298.15$ K and $p = 1$ bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet ?
[Molar mass of $NaHCO_3 = 84$ g mol^{-1}]
(1) 16.8 (2) 8.4
(3) 0.84 (4) 33.6

5. 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solutions respectively are:
(1) 0.167, 11.11 (2) 0.2, 22.20
(3) 0.2, 11.11 (4) 0.167, 22.20

Chapter 2
Redox Reaction

6. Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y, is:-
(1) 5 (2) 3
(3) 1 (4) 7

Chapter 3
Stoichiometry

7. In the reaction of oxalate with permagnate in acidic medium, the number of electrons invoved in producing one molecule of CO_2 is:
(1) 10 (2) 2
(3) 1 (4) 5

8. 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution ?
(1) 25 mL (2) 50 mL
(3) 12.5 mL (4) 75 mL

9. The volume strength of 1M H_2O_2 is:
(Molar mass of $H_2O_2 = 34$ g mol^{-1})
(1) 16.8 (2) 11.2
(3) 22.4 (4) 5.6

10. The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing 10^{-3} M $CaSO_4$ is:
(Molar mass of $CaSO_4 = 136$ g mol^{-1})
(1) 100 ppm (2) 50 ppm
(3) 10 ppm (4) 90 ppm

11. 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is:
(1) 40 g (2) 20 g
(3) 80 g (4) 10 g

Chapter 4
Atomic Structure

12. For emission line of atomic hydrogen from $n_i = 8$ to $n_f =$ the plot of wave number ($\bar{\nu}$) against $\left(\frac{1}{n^2}\right)$ will be
(The Rydberg constant, R_H is in wave number unit).
(1) Linear with slope - R_H
(2) Linear with intercept - R_H
(3) Non linear
(4) Linear with slope R_H

13. Which of the following combination of statements is true regarding interpretation of the atomic orbitals ?

I. An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.

II. For a given value of the principal quantum number, the size of the orbit is inversely proportionl to the azimuthal quantum number.

III. According to wave mechanics, the ground state angular momentum is ħ equal to $h/2\pi$

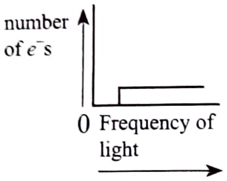
IV. The plot of Ψ vs r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

(1) (II), (III) (2) (I), (IV)

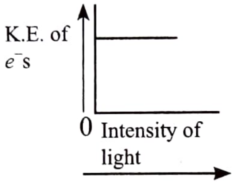
(3) (I), (II) (4) (I), (III)

14. Which of the graph shown below does not represent the relationship between incident light and the electron ejected form metal surface ?

(1)



(2)



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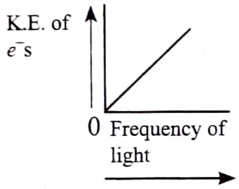

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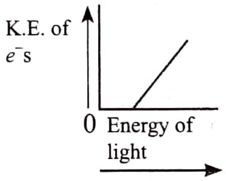


15. The ground state energy of hydrogen atom is –13.6 eV. The energy of second excited state $He^{\oplus}$ ion in eV is:

(1) –6.04 (2) –27.2

(3) –54.4 (4) –3.4

16. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose ?

$[R_H = 1 \times 10^5\ cm^{-1},\ h = 6.6 \times 10^{-34}\ Js,\ c = 3 \times 10^8\ ms^{-1}]$

(1) Paschen, 5 → 3 (2) Paschen, ∞ → 3

(3) Lyman, ∞ → 1 (4) Balmer, ∞ → 2

17. The de Broglie wavelength (λ) associated with a photoelectron varies with the frequency (v) of the incident radiation as, [v_0 is threshold frequency]:

(1) $\lambda \propto \dfrac{1}{(v - v_0)^{\frac{3}{2}}}$ (2) $\lambda \propto \dfrac{1}{(v - v_0)^{\frac{1}{2}}}$

(3) $\lambda \propto \dfrac{1}{(v - v_0)^{\frac{1}{4}}}$ (4) $\lambda \propto \dfrac{1}{(v - v_0)}$

18. If the de Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to 1.5 πa_0(a_0 is Bohr radius), then the value of n/Z is:

(1) 1.0 (2) 0.75

(3) 0.40 (4) 1.50

19. What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity $6 \times 10^5\ ms^{-1}$ form it ?

(Mass of electron = 9×10^{-31} kg

Velocity of light = $3 \times 10^8\ ms^{-1}$

Planck's constant = 6.626×10^{-34} Js

Charge of electron = $1.6 \times 10^{-19}\ J\,eV^{-1}$

(1) 0.9 eV (2) 4.0 eV

(3) 2.1 eV (4) 3.1 eV

Chapter 5
States of Matter

20. 0.5 moles of gas A and X moles of gas B exert a pressure of 200 Pa in a a container of volume 10 m^3 at 1000 K. Given is the gas constant in $JK^{-1}\ mol^{-1}m$, X is:

(1) $\dfrac{2R}{4+12}$ (2) $\dfrac{2R}{4-12}$

(3) $\dfrac{4-R}{2R}$ (4) $\dfrac{4+R}{2R}$

21. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is:

(1) 750°C (2) 500°C

(3) 750 K (4) 500 K

22. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressure of the gases for equal number of moles are :

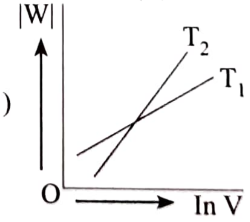
(1) $2P_A = 3P_B$ (2) $P_A = 3P_B$

(3) $P_A = 2P_B$ (4) $3P_A = 2P_B$

Chapter 6
Thermodynamics

23. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperature T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is:

(1)



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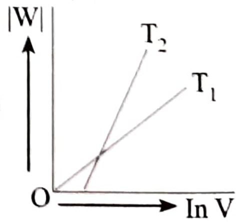
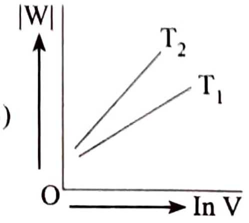


(3)



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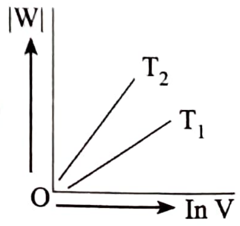


24. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is;
(Specific heat of water liquid and water vapour are 4.2 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1}; heat of liquid fusion and vapourisation of water are 344 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively).
(log 273 = 2.436, log 373 = 2.572, log 383 = 2.583)
(1) 7.90 kJ kg^{-1} K^{-1} (2) 2.64 kJ kg^{-1} K^{-1}
(3) 8.49 kJ kg^{-1} K^{-1} (4) 4.26 kJ kg^{-1} K^{-1}

25. A process has $\Delta H = 200$ $Jmol^{-1}$ and $\Delta S = 40$ JK^{-1} mol^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous :
(1) 5 K (2) 4 K
(3) 20 K (4) 12 K

26. An ideal gas undergoes isothermal compression from 5 to 1m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol^{-1} K^{-1}, the temperature of Al increases by:
(1) $\frac{3}{2}$ K (2) $\frac{2}{3}$ K
(3) 1 K (4) 2 K

27. The process with negative entropy change is :
(1) Dissolution of iodine in water
(2) Synthesis of ammonia from N_2 and H_2
(3) Dissolution of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(4) Sublimation of dry ice

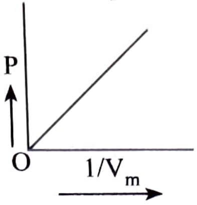
28. Two blocks of the same metal having same mass and at temperature T_1 and T_2, respectively. are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is:
(1) $2C_P \ln\left(\frac{T_1+T_2}{4T_1T_2}\right)$ (2) $2C_P \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$
(3) $C_P \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$ (4) $2C_P \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$

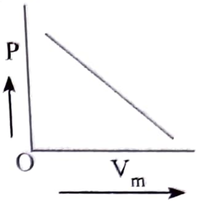
29. $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_r H° = +491.1$ kJ mol^{-1} and $\Delta_r S° = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is:
(1) 1890.0 K (2) 2480.3 K
(3) 2040.5 K (4) 2380.5 K

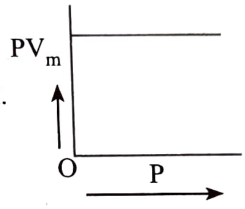
30. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by
$\Delta_r G° = A - Bt$
Where A and B are non-zero constants. Which of the following is TRUE about this reaction ?
(1) Exothermic if $B < 0$
(2) Exothermic if $A > 0$ and $B < 0$
(3) Endothermic if $A < 0$ and $B > 0$
(4) Endothermic if $A > 0$

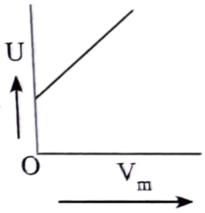
31. For the equilibrium,
$2H_2O \rightleftharpoons H_3O^{\oplus} + \overset{\ominus}{O}H$, the value of $\Delta G°$ at 298 K is approximately :-
(1) –80 kJ mol^{-1} (2) –100 kJ mol^{-1}
(3) 100 kJ mol^{-1} (4) 80 kJ mol^{-1}

32. The combination of plots which does not represent isothermal expansion of an ideal gas is:

I.


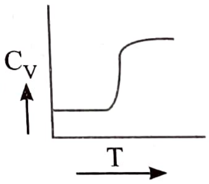
II.


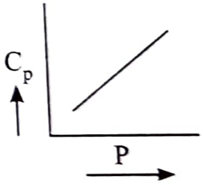
III.


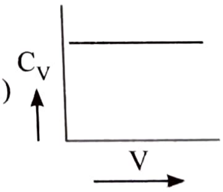
IV.


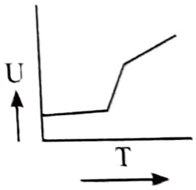
(1) (I) and (III) (2) (I) and (IV)
(3) (II) and (IV) (4) (II) and (III)

33. For diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities ?

(1)


(2)


(3)


(4)


Chapter 7
Chemical Equilibrium

34. Consider the following reversible chemical reaction:
$A_2(g) + B_2(g) \xrightleftharpoons{K_1} 2AB(g)$ ...(1)
$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 2B_2(g)$ ..(2)
The relation between K_1 and K_2 is:
(1) $K_2 = K_1^{\ 3}$ (2) $K_2 = K_1^{-3}$
(3) $K_1K_2 = 3$ (4) $K_1K_2 = 1/3$

35. The value of K_p/K_C for the following reactions at 300 K are, respectively:
(At 300 K, RT = 24.62 dm^3atm mol^{-1})
i. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

ii. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

iii. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(1) 1, 24.62 $dm^3 atm\ mol^{-1}$, 606.0 $dm^6 atm^2\ mol^{-2}$

(2) 1, 4.1×10^{-2} $dm^{-3} atm^{-1}\ mol^{-1}$, 606.0 $dm^6\ atm^2\ mol^{-2}$

(3) 1, 606.0 $dm^6\ atm^2\ mol^{-2}$, 1.65×10^{-3} $dm^3 atm^{-1}\ mol^{-1}$

(4) 1, 24.62 $dm^3\ atm\ mol^{-1}$, 1.65×10^{-3} $dm^{-6}\ atm^{-2}\ mol^2$

36. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH is decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is ($R = 0.082$ L atm $mol^{-1}K^{-1}$, Molar mass of $S = 32$ g mol^{-1}, molar mass of $N = 14$ g mol^{-1})

(1) 1×10^{-4} atm^2

(2) 4.9×10^{-3} atm^2

(3) 0.242 atm^2

(4) 0.242×10^{-4} atm^2

37. Consider the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The equilibrium constant of the above reactoin is K_P. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by

(Assume that $P_{NH_3} << P_{total}$ at equilibrium)

(1) $\dfrac{3^{\frac{3}{2}} K_P^{\frac{1}{2}} P^2}{4}$

(2) $\dfrac{3^{\frac{3}{2}} K_P^{\frac{1}{2}} P^2}{16}$

(3) $\dfrac{K_P^{\frac{1}{2}} P^2}{16}$

(4) $\dfrac{K_P^{\frac{1}{2}} P^2}{4}$

38. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as:

$\Delta_r G°$ (in kJ mol^{-1}) $= 120 - \frac{3}{8}T$

The major component of the reaction mixture at T is:

(1) X if T = 315 K

(2) X if T = 350 K

(3) Y if T = 300 K

(4) Y if T = 280 K

39. In a chemical reaction, $A + 2B \overset{K}{\rightleftharpoons} 2C + D$, the initial concentration of B was 1.5 times of A, but the equilibrium concentration of A, and B were found to be equal. The equilibrium constant(K) for the said chemical reaction is:

(1) 16

(2) 4

(3) 1

(4) 1/4

40. Two solids dissociate as follows

$A(s) \rightleftharpoons B(g) + C(g)$; $K_{p_1} = x\ atm^2$

$D(s) \rightleftharpoons C(g) + E(g)$; $K_{p_2} = y\ atm^2$

The total pressure when both the solids dissociate simultaneously is:-

(1) $x^2 + y^2$ atm

(2) $x^2 - y^2$ atm

(3) $2\left(\sqrt{x+y}\right)$atm

(4) $\sqrt{x+y}$ atm

Chapter 8
Ionic Equilibrium

41. 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is: [pk_b of $NH_4OH = 4.7$].

(1) 9.4

(2) 5.0

(3) 9.0

(4) 5.2

42. A mixture of 100 mmol of $Ca(OH)_2$ and 2g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of $\overset{\ominus}{O}H$ in resulting solution, respectively, are :(Molar mass of $Ca(OH)_2$, Na_2SO_4 and $CaSO_4$ are 74, 143 and 136 g mol^{-1}, respectively; K_{sp} of $Ca(OH)_2$ is 5.5×10^{-6})

(1) 1.9 g, 0.14 mol L^{-1}

(2) 13.6 g, 0.14 mol L^{-1}

(3) 1.9 g, 0.28 mol L^{-1}

(4) 13.6 g, 0.28 mol L^{-1}

43. If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is:

(1) 8×10^{-12} M

(2) 8×10^{-10} M

(3) 8×10^{-11} M

(4) 8×10^{-13} M

Answers Key

Chapter 1

1. (3) **2.** (1) **3.** (1) **4.** (1) **5.** (1)

Chapter 2

6. (1)

Chapter 3

7. (3) **8.** (1) **9.** (2) **10.** (1) **11.** (None)

Chapter 4

12. (4) **13.** (4) **14.** (3) **15.** (1) **16.** (2)
17. (2) **18.** (2) **19.** (3)

Chapter 5

20. (3) **21.** (4) **22.** (1)

Chapter 6

23. (2) **24.** (None) **25.** (1) **26.** (2) **27.** (2)
28. (3) **29.** (2) **30.** (4) **31.** (4) **32.** (3)
33. (2)

Chapter 7

34. (2) **35.** (4) **36.** (3) **37.** (2) **38.** (1)
39. (2) **40.** (3)

Chapter 8

41. (3) **42.** (3) **43.** (2)